

Polymer Synthesis

As discussed in Chapter 1, a useful classification of all polymers is based upon the kinetics of the polymerization. In this classification scheme, a *step-growth* polymerization is defined as one that involves a *random* reaction of two molecules that may be any combination of a monomer, oligomer, or a longer-chain molecule. High-molecular-weight polymer is formed only near the end of the polymerization when most of the monomer has been depleted. In *chain-growth* polymerization, the only chain-extension reaction is that of attachment of a monomer to an "active" chain. The active end may be a free radical or an ionic site (i.e., anion or cation). In contrast to step-growth polymerization, high-molecular-weight polymer is formed in the early stages of a chain-growth polymerization.

2.1 STEP-GROWTH POLYMERIZATION

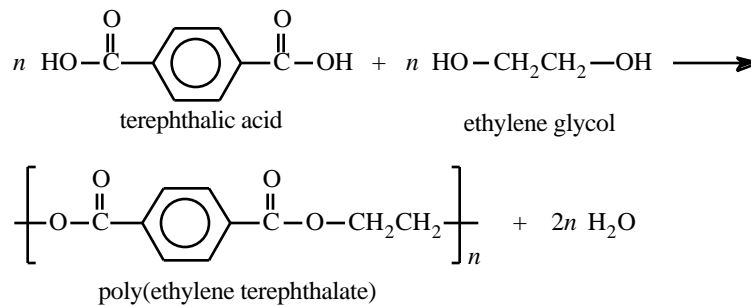
The major classifications of step-growth polymers are given in Table 2-1. Of these, the most important in terms of the size of the commercial market are the aliphatic polyamides or nylons (e.g., nylon-6, nylon-6,6, and nylon-6,10) and polyesters [e.g., poly(ethylene terephthalate)]. Specialty or engineering-grade step-growth polymers include polycarbonate (e.g., Lexan™), aromatic polyamides (e.g., Nomex™ and Kevlar™), polyimides (e.g., Kapton™), polysulfones (e.g., Udel™), polyurethanes, and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO™), as discussed in Chapter 10.

Table 2-1 Classification of Step-Growth Polymers

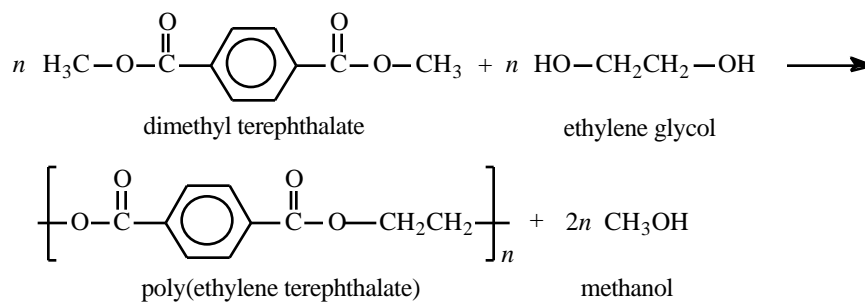
Classification	Monomer 1	Monomer 2
<i>Condensation</i>		
Polyamide	Dicarboxylic acid	Diamine
Polycarbonate	Bisphenol	Phosgene
Polyester	Dicarboxylic acid	Diol or polyol
Polyimide	Tetracarboxylic acid	Diamine
Polysiloxane	Dichlorosilane	Water
Polysulfone	Bisphenol	Dichlorophenylsulfone
<i>Non-condensation</i>		
Polyurethane	Diisocyanate	Diol or polyol
Poly(phenylene oxide)	2,6-Disubstituted phenol	Oxygen

Some examples of commercially important step-growth polymerizations are illustrated in Figure 2-1. Most step-growth polymerizations involve a classical condensation reaction such as esterification (Figure 2-1A), ester interchange (Figure 2-1B), or amidation (Figure 2-1C). Note that two routes exist for the preparation of the aromatic polyester, poly(ethylene terephthalate) (PETP)—polyesterification of terephthalic acid and ethylene glycol (Figure 2-1A) and an ester interchange involving dimethyl terephthalate and ethylene glycol (Figure 2-1B). These polymerizations and the preparation of the aliphatic polyamide, nylon-6,6 (Figure 2-1C), are examples of A~A/B~B step-growth condensation-polymerizations. Each of the two monomers is bifunctional and contains the same functionality at each end (i.e., A or B functional group). For example, PETP may be formed (Figure 2-1A) by the polycondensation of a dicarboxylic acid (terephthalic acid) and a diol (ethylene glycol). Alternately, an aliphatic polyester, polycaprolactone, can be formed by the *self-condensation* of ω -hydroxycaproic acid (Figure 2-1D). Since the functional end groups of this acid are different (i.e., a carboxylic acid and a hydroxyl group at opposite ends), this polyesterification is an example of an A~B step-growth polycondensation.

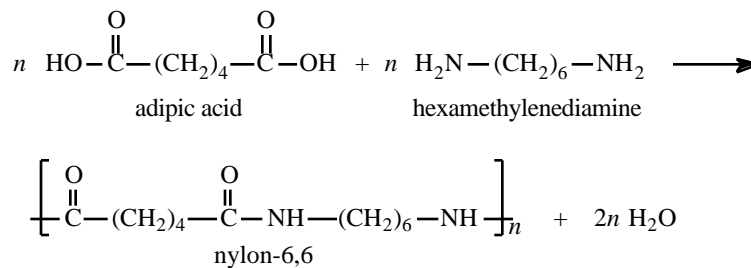
A



B



C



D

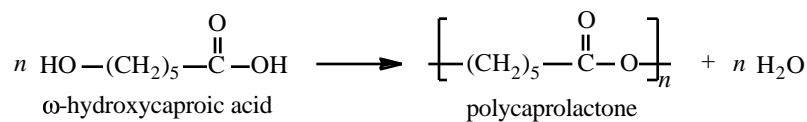
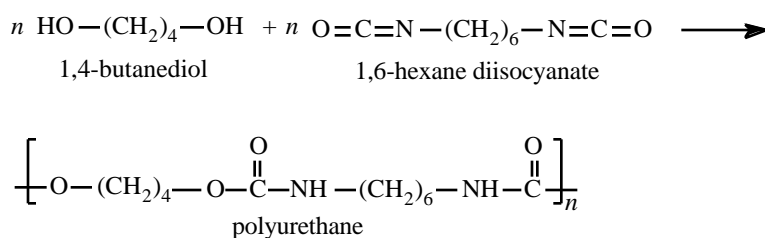


Figure 2-1 Examples of important polycondensations having a step-growth mechanism. **A.** Polyesterification. **B.** Ester-interchange polymerization. **C.** Polyamidation. **D.** Self-condensation of an A-B monomer.

Two *non-condensation*-type step-growth polymerizations are illustrated in Figure 2-2. Figure 2-2A shows the polymerization of a polyurethane prepared by the ionic *addition* of a diol (1,4-butanediol) to a diisocyanate (1,6-hexane diisocyanate). Note that, unlike a conden-

sation polymerization, a small molecule is not liberated as a by-product of this polymerization. Shown in Figure 2-2B is the polymerization of a high-temperature thermoplastic, poly(2,6-dimethyl-1,4-phenylene oxide), by the oxidative-coupling polymerization of 2,6-xylenol. The mechanism of this polymerization is *free radical*, but the kinetics of this and the previous polymerization are distinctly step growth, which means that high-molecular-weight polymer is obtained only at the end of the polymerization. Normally, the kinetics of a free-radical polymerization is chain growth, as will be described in Section 2.2.

A



B

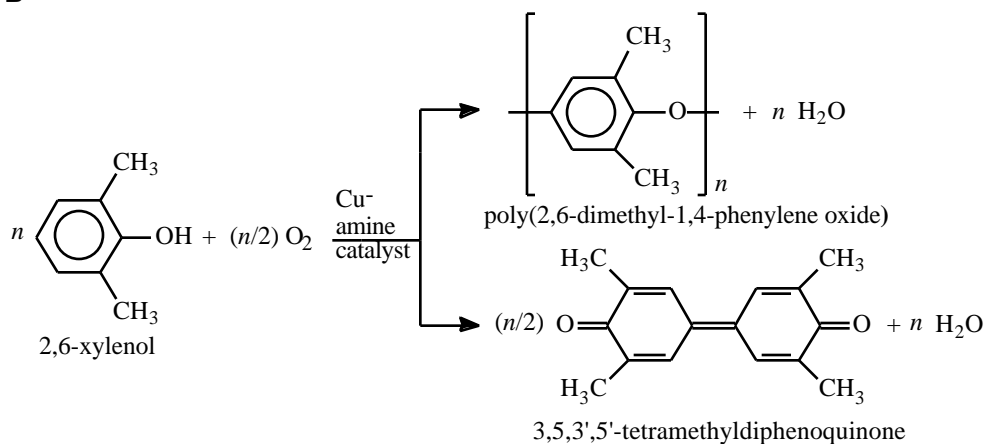


Figure 2-2 Two non-condensation step-growth polymerizations. **A.** Addition polymerization of a polyurethane. **B.** Oxidative-coupling polymerization of 2,6-xylenol to yield a high-molecular-weight polymer or a low-molecular-weight quinone as a by-product.

2.1.1 Molecular Weight in a Step-Growth Polymerization

Polymer molecular weight in a step-growth polymerization is determined by the fractional conversion, p , of the monomer during the polymerization. One way to express molecular

weight is through the *degree of polymerization*, which normally represents the number of repeating units in the polymer chain. Since any polymerization mechanism yields a distribution of molecular weights, it is necessary to define an average degree of polymerization in the same way as average molecular weight was defined earlier (see Section 1.3.2). The average degree of polymerization is designated as \bar{X} or \overline{DP} . The most important averages are the number-average (\bar{X}_n) and weight-average (\bar{X}_w) degrees of polymerization. An equation attributed to Carothers¹ relates the number-average degree of polymerization to fractional monomer-conversion, p , in a step-growth polymerization as (see Example Problem 1.2)[†]

$$\boxed{\bar{X}_n = \frac{1}{1-p}} \quad (2.1)$$

Similarly, the weight-average degree of polymerization is given as

$$\bar{X}_w = \frac{1+p}{1-p} \quad (2.2)$$

These equations do not apply to interfacial polycondensations or to the step-growth polymerization of monomers with a functionality greater than 2. Use of eq. 2.1 indicates that, in order to achieve a typical commercial X_n of 50, a monomer conversion of 98% ($p = 0.98$) must be obtained; for a X_n of 100, the monomer conversion must be 99%. This requirement for high conversion also indicates that a nearly exact stoichiometric equivalence of monomers is required to obtain high monomer conversion in an A~A/B~B polycondensation. Often, this can be achieved by preparing an intermediate low-molecular-weight salt. Sometimes, a slight excess of one monomer is used to control molecular weight.

In addition to high conversion, a step-growth polymerization requires high *yield*. High yield means the absence of any side reactions that could deactivate the polymerization process. For example, a carbon-carbon coupling to give a low-molecular-weight quinone derivative is competitive to the carbon-oxygen coupling polymerization of 2,6-xylenol, as shown in Figure 2-2B. In this case, the yield of the high polymer is determined by the type of catalyst and other polymerization conditions.

High monomer *purity* is also very important in order to obtain high-molecular-weight polymer. In A~A/B~B polycondensation, the incorporation of any monomer that is monofunctional (i.e., having a single A or B group) in the growing polymer chain will terminate

[†] It follows that the number-average molecular weight is given as

$$\bar{M}_n = \frac{M_0}{1-p}$$

where M_0 is the molecular weight of the repeating unit.

the polymerization. An example is the use of a monofunctional amine in place of the diamine in the preparation of nylon-6,6 (Figure 2-1C). Sometimes, a monofunctional monomer may be added during the polymerization process to control molecular weight. Trifunctional monomers can be used to create crosslinked polymers (i.e., thermosets), as will be discussed in Section 9.3.

In summary, high-molecular-weight polymer can be obtained in a step-growth polymerization only if the following conditions are achieved:

- High monomer conversion
- High monomer purity
- High reaction yield
- Stoichiometric equivalence of functional groups (in A~A/B~B polymerization)

2.1.2 Step-Growth Polymerization Kinetics

A step-growth polymerization may be first, second, or third order depending on whether it is an A~B or A~A/B~B type and whether a catalyst is involved. The polymerization rate, R_o , may be expressed as the time rate of change of monomer concentration. For a non-catalyzed A~A/B~B polymerization, this polymerization rate, as defined by the rate of *disappearance* of monomer, is second order in monomer concentration, as given by the expression

$$R_o = -\frac{d[A\sim A]}{dt} = k[A\sim A][B\sim B] \quad (2.3)$$

where k is the polymerization rate constant and the brackets indicate monomer (e.g., A~A or B~B) concentration. Assuming a stoichiometric balance of monomer concentration, eq. 2.3 can be simplified as

$$-\frac{d[A\sim A]}{dt} = k[A\sim A]^2 \quad (2.4)$$

Integration of eq. 2.4 then gives the relation

$$\frac{1}{[A\sim A]} - \frac{1}{[A\sim A]_o} = kt \quad (2.5)$$

where $[A\sim A]_o$ represents the initial monomer-concentration (i.e., at $t = 0$). The non-polymerized monomer concentration at any time t is related to the fractional conversion and initial monomer concentration by

$$[A\sim A] = (1 - p)[A\sim A]_0 \quad (2.6)$$

Rearrangement of eq. 2.6 for $(1 - p)$ and subsequent substitution into the Carothers equation (eq. 2.1) gives

$$\bar{X}_n = \frac{[A\sim A]_0}{[A\sim A]} \quad (2.7a)$$

or

$$[A\sim A] = \frac{[A\sim A]_0}{\bar{X}_n} \quad (2.7b)$$

Substitution of eq. 2.7b into eq. 2.5 and subsequent rearrangement gives the final result

$$\bar{X}_n = [A\sim A]_0 kt + 1 \quad (2.8)$$

2.2 CHAIN-GROWTH POLYMERIZATION

Chain-growth polymerizations require the presence of an initiating molecule that can be used to attach a monomer molecule at the start of the polymerization. The initiating species may be a radical, anion, or cation, as discussed in the following sections. Free-radical, anionic, and cationic chain-growth polymerizations share three common steps—*initiation*, *propagation*, and *termination*. Whether the polymerization of a particular monomer can occur by one or more mechanisms (i.e., free radical, anionic, or cationic) depends, in part, on the chemical nature of the substituent group. In terms of general guidelines, monomers with an *electron-withdrawing* group can polymerize by an anionic pathway, while those with an *electron-donating* group follow a cationic pathway. Some important vinyl monomers such as methyl methacrylate and styrene can be polymerized by more than one pathway (e.g., free-radical and anionic).

2.2.1 Free-Radical Polymerization and Copolymerization

Like other chain-growth polymerizations, a free-radical polymerization has three principal steps:

- Initiation of the active monomer

- Propagation or growth of the active (free-radical) chain by sequential addition of monomers
- Termination of the active chain to give the final polymer product

These steps and their associated kinetics are described next in general terms for free-radical polymerizations, with the polymerization of styrene used as an example.

The Initiation Step. Initiation in a free-radical polymerization consists of two steps—a *dissociation* of the initiator to form two radical species, followed by addition of a single monomer molecule to the initiating radical (the *association* step). The dissociation of the initiator (I~I) to form two free-radical initiator species (I•) can be represented as



where k_d is the *dissociation rate constant*. The dissociation rate constant follows an Arrhenius dependence on temperature given as

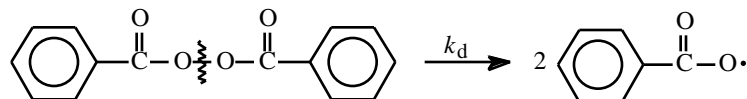
$$k_d = A \exp(-E_a/RT) \quad (2.10)$$

where E_a is the *activation energy* for dissociation. In addition to a strong dependence on temperature, dissociation rate constants for different initiators vary with the nature of the solvent used in solution polymerization, as shown by data given in Table 2-2.

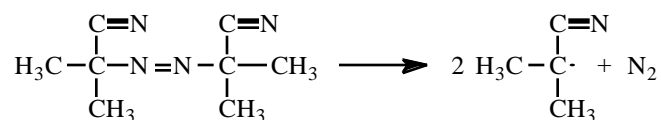
Table 2-2 Dissociation Rate Constants for Some Common Initiators in Solution

Initiator	Solvent	T (°C)	k_d (s ⁻¹)	E_a (kJ mol ⁻¹)
Benzoyl peroxide	Benzene	30	4.80×10^{-8}	116
		70	1.38×10^{-5}	
	Toluene	30	4.94×10^{-8}	121
		70	1.10×10^{-5}	
AIBN	Benzene	40	5.44×10^{-7}	128
		70	3.17×10^{-5}	
	Toluene	70	4.00×10^{-5}	121

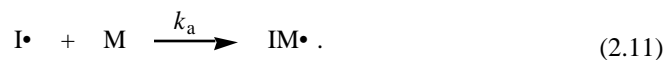
Initiators for free-radical polymerizations include any organic compound with a labile group, such as an azo (–N=N–), disulfide (–S–S–), or peroxide (–O–O–) compound. The labile bond of the initiator can be broken by heat or irradiation, such as UV- or γ -irradiation. An important example of a free-radical initiator is benzoyl peroxide that dissociates as



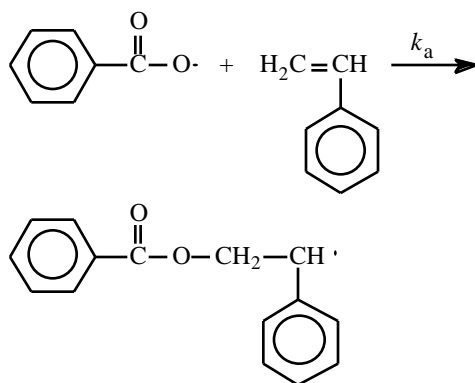
Another important group of free-radical initiators are the azo ($R-N=N-R$) compounds such as 2,2'-azobis(isobutyronitrile) (AIBN), which thermally decomposes to yield nitrogen and two cyanoisopropyl radicals ($R\cdot$) as



In the second step of initiation (i.e., *association*), a monomer molecule (M) is attached to the initiator radical. This addition step may be represented as



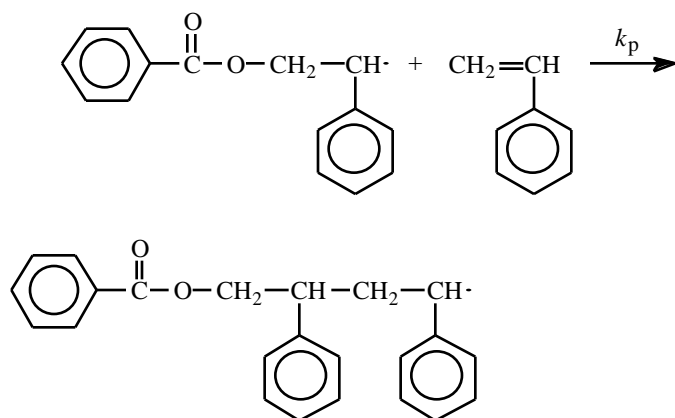
where k_a is the rate constant for monomer association. In the specific case of the polymerization of styrene initiated by benzoyl peroxide, the addition occurs as



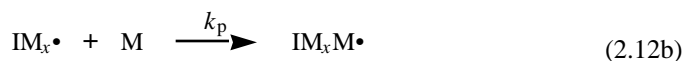
The Propagation Step. In the next step, called *propagation*, additional monomer units are added to the initiated monomer species as



where k_p is the *propagation rate constant*. For styrene addition with benzoyl peroxide initiation, the first propagation step is

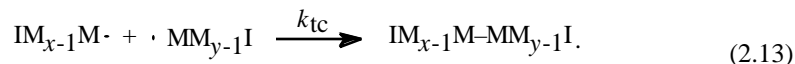


Additional monomers are added sequentially during subsequent propagation steps, as represented by the generalized equation

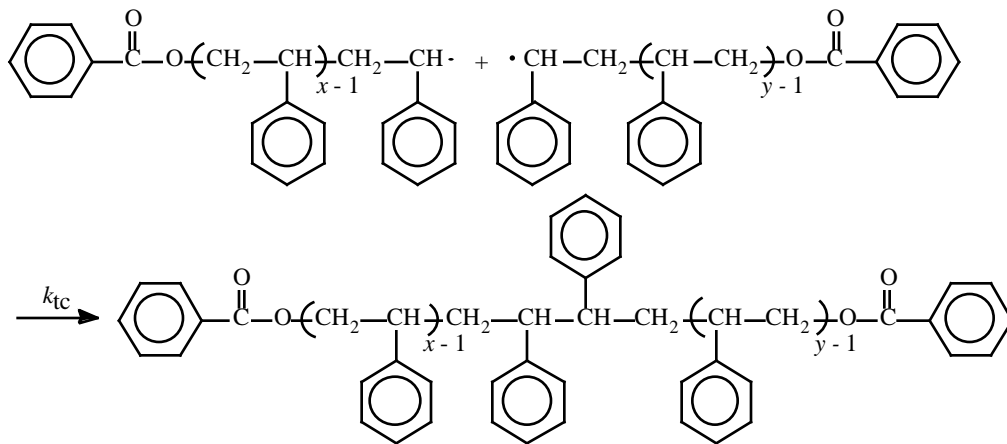


During the propagation step in vinyl polymerization, the energetically preferred placement of monomers is head-to-tail where the more substituted carbon atom is designated as the “head.” Head-to-head placement may occur, for example, during termination by combination as discussed in the next section.

Termination. Propagation will continue until some termination process occurs. One obvious termination mechanism occurs when two propagating radical chains of arbitrary degrees of polymerization of x and y meet at their free-radical ends. Termination in this manner occurs by *combination* to give a single terminated chain of degree of polymerization $x + y$ through the formation of a covalent bond between the two combining radical chains, as illustrated by the following reaction:

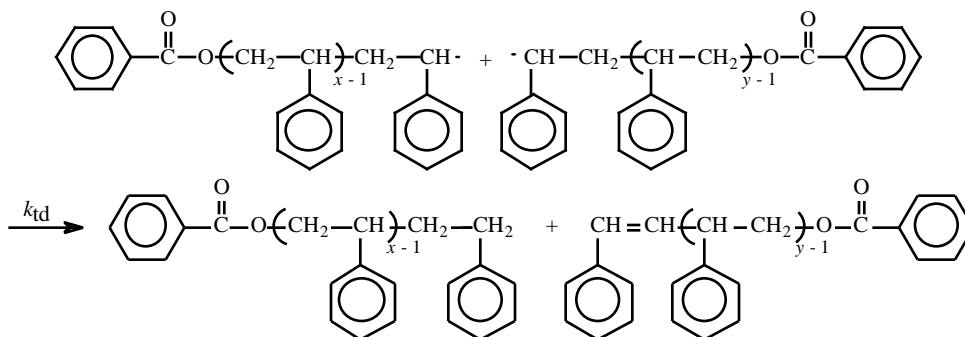
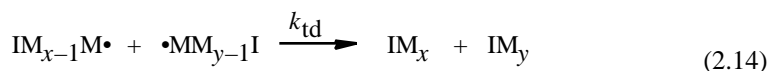


For the example of styrene polymerization, termination by combination gives the following chemical structure:

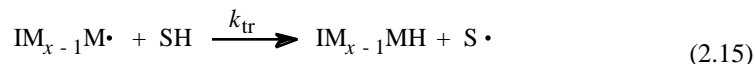


The above structure shows a single head-to-head placement of styrene units at the combination site.

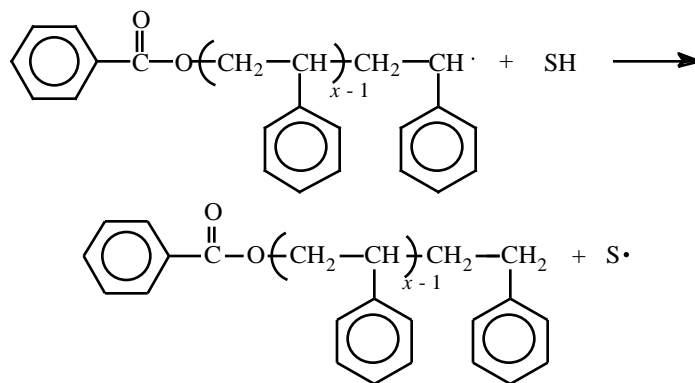
Termination also can occur by a *disproportionation* reaction to give two terminated chains, as illustrated below. In this case, one terminated chain will have an unsaturated carbon group while the other terminated end is fully saturated. In both cases of termination, one end (i.e., in termination by disproportionation) or both ends (i.e., in termination by combination) contain the initiating free-radical group of the initiator molecule. In the case of termination by combination, the benzoyl peroxide group caps *both* ends of the chain. This indicates the important difference between an initiator, which becomes part of the terminated chain, and a polymerization *catalyst*, which promotes the polymerization but is fully recovered at the end of the polymerization. Catalysts are used in cationic and coordination polymerizations as discussed in Sections 2.2.2 and 2.2.3.



In addition to termination by combination and disproportionation, another mechanism of termination is *chain transfer* by hydrogen abstraction from an initiator, monomer, polymer, or solvent molecule. In general terms, this process may be represented as



where SH represents a solvent or any other molecule with an abstractable hydrogen atom. In the specific case of the benzoyl peroxide-initiated polymerization of styrene, termination by chain transfer occurs as



As illustrated, the radical site is transferred to the chain-transfer agent (S \cdot), which can then add monomer units to continue the polymerization process. Subsequent termination of the growing chain-transfer radical chain (SM $_x$ \cdot) will result in a terminated chain having one (i.e., termination by disproportionation) or two (i.e., termination by combination) chain-transfer (S) groups at the polymer ends.

Examples of propagation and termination rate constants are given in Table 2-3. Both k_p and k_t show a strong (Arrhenius) dependence upon temperature, as illustrated by data for styrene. Rate constants can vary by several orders of magnitude depending on monomer type (i.e., vary with the chemical nature of the substituent group in vinyl polymerization).

Free-Radical Polymerization Kinetics. The overall rate of polymerization (R_o) in a free-radical polymerization is simply the rate of chain propagation (R_p), which is obtained from eq. 2.12b as

$$R_o = R_p = k_p [\text{IM}_x\cdot] [\text{M}]. \quad (2.16)$$

This statement makes the assumption that all steps, including the first, in the propagation step have equal reactivity. Compared to step-growth polymerization, the propagation rate for free-radical polymerization is very rapid. Very high-molecular-weight polymer can be formed in less than one second.

Table 2-3 Representative Values of Propagation and Termination Rate Constants

Monomer	T (°C)	k_p (L mol ⁻¹ s ⁻¹)	k_t (L mol ⁻¹ s ⁻¹) × 10 ⁻⁶
Styrene	25	44	48
	30	55	51
	60	176	72
Vinyl acetate	25	1012	59
Vinyl chloride	25	3130	2300
Vinylidene chloride	25	6.6	0.175
Acrylonitrile	25	52	5
Ethylene*	83	470	1050
Methyl methacrylate	40	513	47

* Polymerization in benzene.

One problem with the use of eq. 2.16 to determine the polymerization rate is that the radical concentration, $[M_x \cdot]$, normally is not known. To overcome this difficulty, the radical concentration can be related to more easily-determined concentrations (i.e., monomer and initiator concentrations) by assuming that the total radical population obtains a *steady-state* concentration over most of the polymerization process. Since radicals are formed in the initiation step and consumed in the termination step, the steady-state condition can be expressed as

$$R_i = R_t \quad (2.17)$$

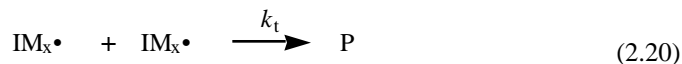
As described previously, the initiation process involves two separate steps—initiator dissociation and monomer association. *The overall rate of initiation is, therefore, controlled by the slower step, which is the dissociation of the initiator.* The rate of initiation, expressed as the time rate of increase in radical-initiator concentration, is then obtained from the dissociation expression (eq. 2.9) as

$$R_i = \frac{d[I \cdot]}{dt} = 2k_d[I] \quad (2.18)$$

where $[I]$ is used to represent the initiator ($I \sim I$) concentration. The factor of 2 appearing on the RHS of eq. 2.18 is due to the fact that *two* radicals are produced in each dissociation step. In order to obtain an expression for the rate of polymerization, it is necessary to consider only those initiator radicals that add monomer and, therefore, contribute to chain propagation. Some initiator radicals may recombine with other radicals (e.g., initiator and monomer radical groups) or partially decompose into non-initiating products. For these reasons, only some fraction, f , of the original initiator concentration is effective in contributing to the polymerization process. Typical initiator efficiencies fall in the range from 0.3 to 0.8 (e.g., $f \sim 0.6$ for AIBN over a wide range of monomer concentration). The fraction of effective initiator-radicals can then be introduced in the rate expression (eq. 2.18) to give

$$R_i = \frac{d[I \cdot]}{dt} = 2fk_d[I]. \quad (2.19)$$

In a similar fashion, the rate of termination is the time-rate of decrease in radical concentration (i.e., the propagating radical-chain) resulting from all operative termination steps—combination (eq. 2.13), dissociation (eq. 2.14), and/or chain transfer (eq. 2.15). For the moment, it is convenient to consider only termination by combination and disproportionation and leave termination by chain transfer for later treatment. Without any loss in generality, termination by both combination and disproportionation can be expressed as



where P represents the *deactivated* polymer and the termination rate constant, k_t , is the sum of the individual termination rate constants of combination and disproportionation (i.e., $k_t = k_{tc} + k_{td}$). Therefore, the termination rate equation can be written for the reaction given in eq. 2.20 as

$$R_t = -\frac{d[IM_x \cdot]}{dt} = 2k_t[IM_x \cdot]^2. \quad (2.21)$$

The factor of 2 arises because two radicals are consumed in each termination step.

Applying the steady-state assumption (eq. 2.17) by equating eqs. 2.19 and 2.21 gives the expression for the radical concentration as

$$[IM_x \cdot] = \frac{fk_d}{k_t} [I]^{1/2}. \quad (2.22)$$

Finally, substitution of eq. 2.22 into the polymerization rate equation (eq. 2.16) gives the following important result:

$$R_p = k_p \frac{fk_d}{k_t} [I]^{1/2} [M] \quad (2.23)$$

Equation 2.23 shows that the polymerization rate in free-radical polymerization is proportional to monomer concentration and to the square-root of initiator concentration.[†]

The number-average degree of polymerization at any time can be obtained from the ratio of the rate of propagation to the rate of termination as[‡]

$$\bar{X}_n = \frac{R_p}{R_t} \quad (2.24)$$

which at steady state is given (from eqs. 2.16, 2.21, and 2.22) as

$$\bar{X}_n = \frac{k_p [M]}{2(k_t f k_d [I])^{1/2}} \quad (2.25)$$

[†] It is important to recognize that eq. 2.23 gives the polymerization rate at some arbitrary time t when the initiator and monomer concentrations are $[I]$ and $[M]$ at that time. These concentrations differ from their initial concentrations, $[I]_0$ and $[M]_0$, which are known at the beginning of the polymerization. The relationships between $[I]$ and $[I]_0$ and between $[M]$ and $[M]_0$ are obtained from the appropriate rate equations. For example, the initiator concentration is obtained from the rate of dissociation obtained from eq. 2.9 as

$$-\frac{d[I]}{dt} = k_d [I].$$

Rearrangement and integration of the above equation from $t = 0$ to time t gives

$$[I] = [I]_0 \exp(-k_d t).$$

Similarly, monomer concentration is obtained from the propagation step (eq 2.12b) as

$$-\frac{d[M]}{dt} = k_p [IM_x \cdot] [M]$$

which upon integration gives

$$[M] = [M]_0 \exp(-k_p [IM_x \cdot] t)$$

where $[IM_x \cdot]$ can be obtained from $[I]$ by means of eq. 2.22.

[‡] Alternately, a *kinetic chain length*, ν , may be defined as the average number of steps of growth per effective radical given as the ratios of the propagation and initiation rates as $\nu = R_p / R_i$.

In the above derivations, we have considered only termination by combination and disproportionation. If termination by chain transfer can also occur, the degree of polymerization (eq. 2.24) must be modified to include this contribution to the termination rate. As the chain-transfer process increases the overall rate of termination, it is clear from eq. 2.24 that the degree of polymerization, therefore, should decrease. We can write the number-average degree of polymerization in the case of termination by all three termination mechanisms as

$$\bar{X}_n = \frac{R_p}{R_{tc} + R_{td} + R_{tr}} \quad (2.26)$$

where R_{tr} is the rate of termination by chain transfer obtained from eq. 2.15 as

$$R_{tr} = k_{tr} [\text{IM}_x \cdot] [\text{SH}]. \quad (2.27)$$

Rearrangement of eq. 2.26 and substitution of the rate equation for R_{tr} (eq. 2.27) and that for R_p (eq. 2.16) gives

$$\frac{1}{\bar{X}_n} = \frac{1}{(\bar{X}_n)_o} + C \frac{[\text{SH}]}{[\text{M}]} \quad (2.28)$$

where $(\bar{X}_n)_o$ is the number-average degree of polymerization in the absence of chain transfer (i.e., eq. 2.24) and C is the *chain-transfer coefficient* given as

$$C = \frac{k_{tr}}{k_p}. \quad (2.29)$$

Representative values of chain-transfer constants for several common monomers and chain-transfer agents (i.e., initiator, monomer, polymer, solvent, or additive) are given in Table 2-4. As indicated by the form of eq. 2.28, molecular weight will decrease with an increase in the concentration of a chain-transfer agent.

Thermodynamics of Free-Radical Polymerization. The Gibbs free energy of polymerization, G_p , is given by the first and second laws of thermodynamics for a reversible process as

$$G_p = H_p - T S_p \quad (2.30)$$

where H_p is called the *heat of polymerization* defined as

$$H_p = E_{dp} - E_p \quad (2.31)$$

where E_{dp} and E_p are the activation energies for depolymerization[†] and propagation[‡], respectively. Both H_p and S_p are negative and, therefore, G_p also will be negative (i.e., polymerization is favored) at low to moderate temperatures. As temperature increases, G_p becomes less negative (i.e., less favorable). At some temperature, called the *ceiling temperature* (T_c), the polymerization reaches equilibrium. In other words, the rates of polymerization and depolymerization become equal and

$$G_p = 0 \quad (2.32)$$

Table 2-4 Representative Values of Chain-Transfer Constants

Monomer	Chain-Transfer Agent	T (°C)	$C \times 10^4$
Styrene	Styrene	25	0.279
		50	0.35–0.78
	Polystyrene	50	1.9–16.6
	Benzoyl peroxide	50	0.13
	Toluene	60	0.125
Methyl methacrylate	Methyl methacrylate	30	0.117
		70	0.2
	Poly(methyl methacrylate)	50	0.22–1000
	Benzoyl peroxide	50	0.01
	Toluene	40	0.170

The ceiling temperature is then obtained from eq. 2.30 as

$$T_c = \frac{H_p}{S_p} \quad (2.33)$$

Representative values of H_p and T_c for some common monomers are given in Table 2-5.

[†] $k_{dp} = A_{dp} \exp(-E_{dp}/RT)$.

[‡] $k_p = A_p \exp(-E_p/RT)$.

Table 2-5 Heats of Polymerization and Ceiling Temperatures

Monomer	ΔH_p (kJ mol ⁻¹)	T_c (°C)
α -Methystyrene	-35	61
Methyl methacrylate	-55	220
Propylene	-69	300
Styrene	-69	310
Ethylene	-94	400

Free-Radical Copolymerization. As illustrated in Figure 2-3, four separate propagation steps are possible in a free-radical copolymerization. Each propagation step has its own rate constant k_{ij} , where the first subscript, i , identifies the monomer at the end of the propagating chain (i.e., $\sim\sim\sim M_i \cdot$) prior to addition of monomer j . The rates of disappearance of comonomers M_1 and M_2 can be obtained by considering the individual steps by which M_1 (see propagation steps A and C) and M_2 (see propagation steps B and D) are consumed. The rate equations are, therefore, given as

$$\frac{-d[M_1]}{dt} = k_{11}[\sim\sim\sim M_1 \cdot][M_1] + k_{21}[\sim\sim\sim M_2 \cdot][M_1] \quad (2.34)$$

and

$$\frac{-d[M_2]}{dt} = k_{12}[\sim\sim\sim M_1 \cdot][M_2] + k_{22}[\sim\sim\sim M_2 \cdot][M_2]. \quad (2.35)$$

In the case of a terpolymerization (three monomers), the number of propagation steps would increase from four to nine and *three* separate rate equations would be needed.

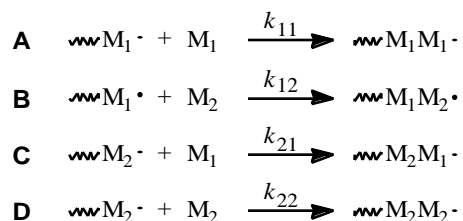


Figure 2-3 The four propagation steps that can occur during a free-radical copolymerization.

During a copolymerization it is important to be able to predict how copolymer composition varies as a function of comonomer reactivity and concentration at any time. The approach used relies on the realization that a monomer consumed during the copolymerization becomes incorporated into the copolymer structure and, therefore, any relative change in the composition of the comonomer mixture reflects the composition of the copolymer formed at that instance of time. The relative change in the comonomer composition is given by the *instantaneous copolymerization equation*, which is obtained by dividing eq. 2.34 by eq. 2.35 to give

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{k_{11} [\text{---}M_1\cdot] + k_{21} [\text{---}M_2\cdot]}{k_{12} [\text{---}M_1\cdot] + k_{22} [\text{---}M_2\cdot]} \quad (2.36)$$

Equation 2.36 can be expressed in a more concise and useful form by defining a monomer *reactivity ratio*. The reactivity ratios for monomers 1 and 2 are defined as

$$r_1 = \frac{k_{11}}{k_{12}} \quad (2.37)$$

and

$$r_2 = \frac{k_{22}}{k_{21}} \quad (2.38)$$

These expressions indicate that the reactivity ratio for monomer 1, r_1 , is simply the ratio of the propagation rate constants for the addition of M_1 (i.e., homopolymerization) and addition of M_2 (i.e., copolymerization) to a propagating radical-chain with monomer 1 at the radical end ($\text{---}M_1\cdot$). Similarly, the reactivity ratio for monomer 2 is the ratio of the propagation rate constants for the addition of M_2 (i.e., homopolymerization) and addition of M_1 (i.e., copolymerization) to a propagating radical-chain with monomer 2 at the radical end ($\text{---}M_2\cdot$). The definitions of reactivity ratios (eqs. 2.37 and 2.38) indicate that when both reactivity ratios equal unity, there is no preferential monomer incorporation into the propagating chain (i.e., $k_{11} = k_{12}$ and $k_{22} = k_{21}$). This means that the monomer sequence in the resulting copolymer is completely *random*. An example of a nearly random or "ideal" copolymerization is that of styrene and 4-chlorostyrene (see Problem 2.4). When both reactivity ratios are zero (i.e., $k_{11} = k_{22} = 0$), the monomer sequence will be *alternating*, as approximately the case for the copolymerization of styrene and maleic anhydride. If both reactivity ratios are small but not exactly zero, the comonomer sequence will not be completely alternating but will have an alternating tendency (i.e., segments of alternating sequences). An

example is the commercially important copolymers of styrene and acrylonitrile. On the other hand, when *both* reactivity ratios are very much larger than unity (i.e., $k_{ii} \gg k_{ij}$), only block copolymers or a mixture of the two homopolymers will form.

Reactivity ratios have been determined for many important combinations of monomers and have been tabulated in several reference sources, such as the *Polymer Handbook*.² Some representative values are given in Table 2-6. Reactivity ratios for less common monomer-pairs can be calculated by means of the *Q-e* scheme proposed by Alfrey and Price.³ In this approach, the propagation rate constant, k_{ij} , is defined as

$$k_{ij} = P_i Q_j \exp(-e_i e_j) \quad (2.39)$$

where P_i is a proportionality constant, Q_j is a measure of the monomer reactivity, and e is the polarity of the radical $M_1 \cdot$ or $M_2 \cdot$. It then follows from the definition of the reactivity ratios (eqs. 2.37 and 2.38) that

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)] \quad (2.40)$$

and

$$r_2 = \frac{k_{22}}{k_{21}} = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)]. \quad (2.41)$$

Values of Q and e also have been tabulated for many monomers.² Table 2-7 gives values for some commercially important monomers. Values of Q and e are referenced to styrene, the most common comonomer, for which Q is set to 1.0. In general, the value of a reactivity ratio is independent of the nature of the initiator and solvent in a free-radical copolymerization; however, there is a weak dependence on temperature.

A limitation of the copolymerization equation as written in eq. 2.36 is the use of radical-chain concentrations, which are usually not known or easily measured. By using the definitions of reactivity ratios and by assuming a steady-state concentration of radicals for either $\overline{M}_1 \cdot$ and $\overline{M}_2 \cdot$ during propagation, the instantaneous copolymerization equation (eq. 2.36), as first derived by Mayo and Lewis,⁴ becomes

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \quad (2.42)$$

Since the relative rate of monomer disappearance is equal to the relative rate of monomer incorporation, eq. 2.42 can be used to estimate copolymer composition when the reactivity ratios are known. Conversely, knowledge of monomer concentration and determination of the copolymer composition can be used to obtain experimental values for the reactivity ratios.

Table 2-6 Examples of Reactivity Ratios for Free-Radical Copolymerization

Monomer 1	Monomer 2	r_1	r_2
Ethylene	Vinyl acetate	0.130	1.230
	Carbon monoxide	0.025	0.004
	Propylene	3.200	0.620
Styrene	Acrylonitrile	0.290	0.020
	Butadiene	0.820	1.380
	Divinylbenzene	0.260	1.180
	Maleic anhydride	0.097	0.001
	Methyl methacrylate	0.585	0.478
	4-Chlorostyrene	0.816	1.062
	Vinylidene chloride	1.700	0.110
Vinyl chloride	Vinylidene chloride	0.205	3.068

Table 2-7 Q-e Values for Free-Radical Copolymerization

Monomer	Q	e
Acrylamide	0.23	0.54
Acrylonitrile	0.48	1.23
Butadiene	1.70	-0.50
Ethylene	0.016	0.05
Isobutylene	0.023	-1.20
Isoprene	1.99	-0.55
Maleic anhydride	0.86	3.69
Methacrylic acid	0.98	0.62
Methyl methacrylate	0.78	0.40
N-Vinyl pyrrolidone	0.088	-1.62
Styrene	1.00	-0.80
Vinyl acetate	0.026	-0.88
Vinyl chloride	0.056	0.16
Vinylidene chloride	0.31	0.34

The copolymerization equation (eq. 2.42) may be recast in an alternative form that is useful for calculating the instantaneous copolymer composition for a given monomer concentration. For this purpose, the mole fraction of monomer 1 in the monomer mixture is defined as

$$f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad (2.43)$$

where $f_1 + f_2 = 1$. In a similar fashion, the mole fraction of monomer 1, F_1 , in the copolymer is given by the relative differential change in monomer concentration as

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad (2.44)$$

where $F_1 + F_2 = 1$. If the numerator and denominator of eq. 2.44 are each divided by $d[M_2]$, use of eqs. 2.42 and 2.43 give the following useful relationship:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (2.45)$$

An illustration of several possible relationships between f_1 and F_1 is given by Figure 2-4. Use of eq. 2.45 indicates that $F_1 = f_1$ when $r_1 = r_2 = 1$. This is the limiting case of *ideal* or random copolymerization illustrated by the dashed line in Figure 2-4. Inspection of eq. 2.45 also indicates that $F_1 = 0.5$ when $r_1 = r_2 = 0$. In this case, the copolymer sequence is always *alternating* and is, therefore, *independent of the comonomer concentration of the feed* as indicated by the horizontal broken line in Figure 2-4. An example of a copolymerization that is intermediate between these two extremes of ideal and alternating copolymerization is that of styrene and methyl methacrylate, illustrated by the curve in Figure 2-4. In such cases, which are neither ideal (i.e., random) or perfectly alternating, the most reactive monomer will be preferentially consumed. This means that the monomer feed composition will change (i.e., drift) with time. If this drift is appreciable, the product copolymer obtained at high monomer conversion will be a heterogeneous mixture of individual copolymers having different compositions. This heterogeneity can lead to undesirable properties such as low mechanical strength due to phase separation in the solid state. To avoid significant drift, copolymerization conversion can be kept low. Unfortunately, low conversion results in high costs for copolymer recovery. In commercial practice, the more rapidly depleted monomer may be continuously added to the copolymerization mixture to maintain a constant feed composition. As shown in Figure 2-4, there is a composition, an *azeotrope*, in analogy to a batch distillation, where the curve crosses over the ideal composition line and the copolymer

will have the same composition as the feed. A product of constant composition will, therefore, be obtained by operating at the azeotrope.

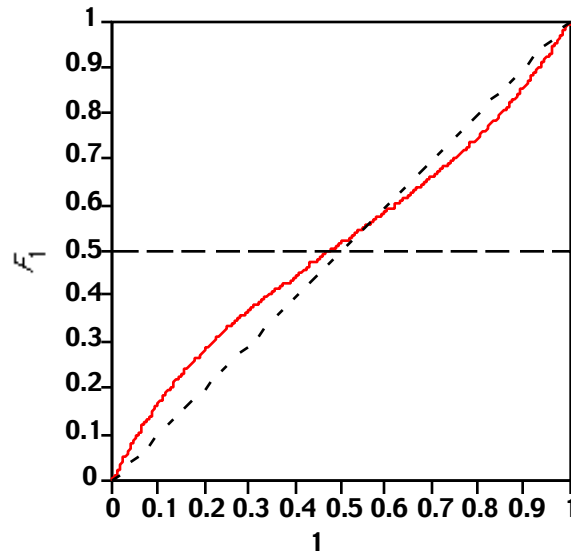
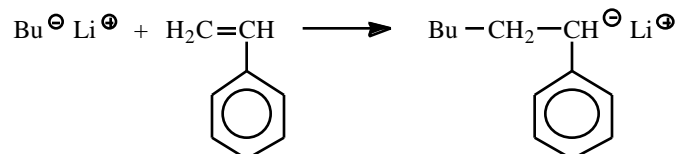


Figure 2-4 Plot of mole fraction of monomer 1 in the copolymer, F_1 , versus mole fraction of monomer 1 in the feed, f_1 , for (---) ideal ($r_1 = r_2 = 1$), (-·-) alternating ($r_1 = r_2 = 0$), and (—) partially alternating copolymerization (the copolymerization of styrene and methyl methacrylate, where $r_1 = 0.585$ and $r_2 = 0.478$).

2.2.2 Ionic Polymerization and Copolymerization

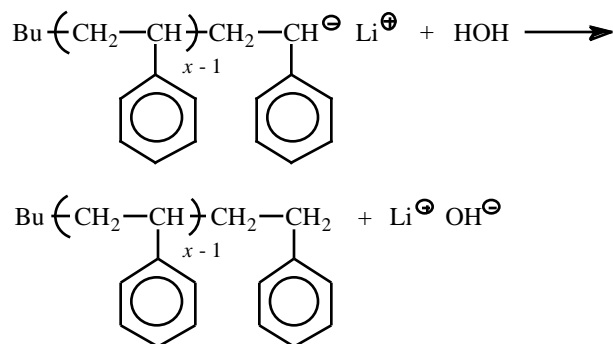
Ionic polymerizations follow the same basic steps as free-radical chain-growth polymerization (i.e., initiation, propagation, and termination); however, there are some important differences, as will be discussed in the following sections. Either a carbanion (C^{\ominus}) or carbonium (C^{\oplus}) ionic site can be formed in the initiation process. Polymerization of vinyl monomers with an electron-withdrawing group can proceed by an anionic pathway, while monomers with an electron-donating group (e.g., methyl) can polymerize by a cationic mechanism.

Anionic Polymerization. The initiator in an anionic polymerization may be any strong nucleophile, including Grignard reagents[†] and other organometallic compounds like *n*-butyl (*n*-C₄H₉) lithium. As an example, the anionic initiation of styrene is illustrated next:



During the initiation process, the addition of the butyl anion to styrene produces a carbanion at the head end in association with the positively-charged lithium *counterion*. The chain propagates by insertion of additional styrene monomers between the carbanion and counterion.

If the starting reagents are pure and if the polymerization reactor is purged of all oxygen and traces of water, propagation can proceed indefinitely or until all monomer is consumed. For this reason, anionic polymerization is sometimes called "living" polymerization.⁵ In this case, termination occurs only by the deliberate introduction of oxygen, carbon dioxide, methanol, or water as follows:



Note that the initiating species in this example (*n*-C₄H₉) has been incorporated as an end group of the terminated polymer-chain. This illustrates the role of butyl-lithium as an initiator — rather than a catalyst — as was also the case for benzoyl peroxide in the free-radical polymerization of styrene.

In the absence of a termination mechanism, each monomer in an anionic polymerization has an equal probability of attaching to an anionic site. Therefore, the number-average

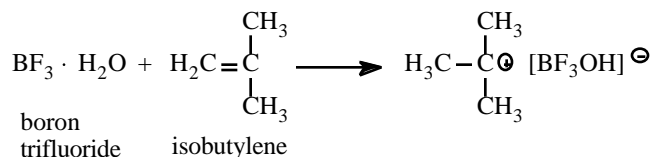
[†] The chemical formula of a Grignard reagent can be expressed as RMgX, where R may be an alkyl, aryl, or other organic group and X is a halogen, especially Cl, Br, or I.

degree of polymerization, \bar{X}_n , is simply equal to the ratio of initial monomer to initial initiator concentration as

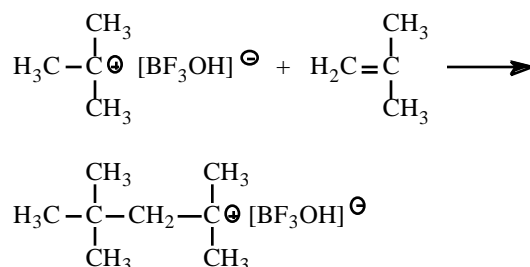
$$\bar{X}_n = \frac{[M]_0}{[I]_0} \quad (2.46)$$

The absence of termination during a living polymerization leads to a very narrow-molecular-weight distribution with polydispersities (see Section 1.3.2) as low as 1.06. By comparison, polydispersities above 2 and as high as 20 are typical in free-radical polymerization.

Cationic Polymerization. Unlike free-radical and anionic polymerizations, initiation in cationic polymerization employs a true catalyst that is restored at the end of the polymerization and does not become incorporated into the terminated polymer chain. Any strong Lewis acid[†] like boron trifluoride (BF₃) can be used as a catalyst. In this case, a *co-catalyst* (e.g., water) is required as the actual proton source. Cationic initiation is illustrated next for the commercially important example of isobutylene polymerization.



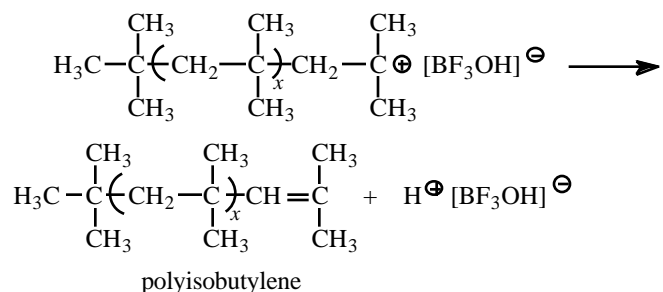
In the above case, proton addition yields an isobutylene *carbonium* ion that forms an association with a BF₃•OH counterion or *gegen* ion. The carbonium ion can then add to the double bond of another isobutylene molecule during propagation, as follows:



Unlike the case of free-radical polymerization, termination by combination of two cationic polymer chains cannot occur. In certain cationic polymerizations, a distinct termina-

[†] A Lewis acid is formally defined as an electron acceptor such as H⁺, BF₃, or AlCl₃.

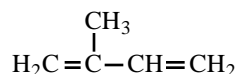
tion step may not take place (i.e., "living" cationic polymerization); however, *chain transfer* to a monomer, polymer, solvent, or counterion will usually occur. The process of chain transfer to the counterion is



As this termination step shows, the catalyst and co-catalyst are restored at the end of the polymerization.

Cationic polymerizations are usually conducted in solution and often at low temperature, typically -80° to -100°C , which provides satisfactory polymerization rates. The choice of solvent for cationic polymerizations is important because of the importance of solvent to the strength of the association between cation and counterion. A "tight" association will prevent monomer insertion during propagation. Typically, there is a linear increase in polymer chain-length and an exponential increase in polymerization rate as the dielectric strength of the solvent increases.

Ionic Copolymerization. As in the case of free-radical copolymerization, two or more monomers can be copolymerized by an ionic mechanism. For example, the commercial elastomer of polyisobutylene (butyl rubber) is a copolymer obtained by the cationic copolymerization of isobutylene with 0.5% to 2% of isoprene (2-methyl-1,3-butadiene).



The comonomer, isoprene, provides unsaturated sites for vulcanization (see Section 9.2.1).

Another important example of an ionic copolymerization is the triblock copolymer SBS, which has a central butadiene block with a styrene blocks at each end of the chain. This triblock copolymer is an example of a thermoplastic elastomer that is elastic at ambient temperature but can be molded like other thermoplastics at higher temperatures. It can be prepared by adding styrene monomer to an active butadiene chain having anionic sites at both ends (i.e., a butadiene dianion). The dianion is obtained by using an electron-transfer initiator such as sodium naphthalenide prepared by reacting naphthalene with sodium as shown in Figure 2-5A. The naphthalene radical-anion can transfer an electron to the monomer (butadiene) to form a monomer radical-anion, as illustrated in Figure 2-5B. Two radical anions can

then combine to give a dimer with carbanion sites at opposite ends, as illustrated in Figure 2-5C. The carbanion sites are then available for addition of more butadiene monomers to obtain a predetermined degree of polymerization. At that point, styrene monomer can be added to form the SBS triblock copolymer.

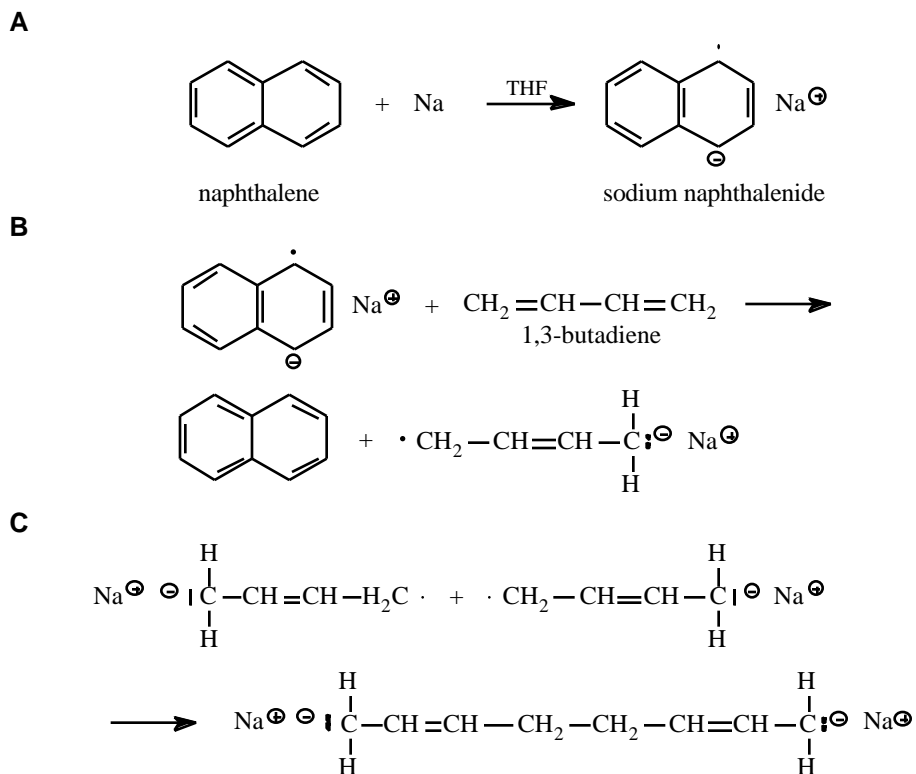


Figure 2-5 Use of sodium naphthalenide in the synthesis of a SBS triblock copolymer. **A.** Formation of sodium naphthalenide from naphthalene and sodium. **B.** Reaction of sodium naphthalenide with butadiene monomer. **C.** Combination of radicals to give the dianion available for anionic polymerization at both ends.

2.2.3 Coordination Polymerization

One of the earliest and most important groups of thermoplastics is the polyolefins—polyethylene and polypropylene (see Section 9.1.1). In 1939, a high-pressure, free-radical process was developed at ICI in England to polymerize ethylene. This polymer had a

—CH₂—CH₂— backbone with some short and long alkane branches. Crystallinity was moderate and both thermal and mechanical properties were suitable for film and bottle applications. Today, this particular grade of polyethylene is called low-density polyethylene (LDPE) and is among the most important commodity thermoplastics. In contrast, free-radical polymerization of propylene yields an amorphous polymer that is a tacky gum at room temperature and has no significant commercial use. It was not until 1954, through the work of Giulio Natta⁶ in Italy, that a stereochemical process was developed to synthesize *isotactic* polypropylene (*i*-PP). This form of polypropylene had a level of crystallinity comparable to LDPE and exhibited good mechanical properties over a wide range of temperatures. A process similar to that used in the production of *i*-PP was developed by Karl Ziegler⁷ in Germany to polymerize ethylene at substantially lower temperature and pressure than required to reduce the extent of branching occurring during the free-radical polymerization of ethylene. This polyethylene—high-density polyethylene (HDPE)—had fewer branches and, therefore, could obtain a higher degree of crystallinity than LDPE. For their work in developing these processes, Ziegler and Natta shared the 1963 Nobel prize in chemistry.

The processes used in the polymerization of both *i*-PP and HDPE employ a novel class of transition-metal catalysts, called Ziegler–Natta (Z–N) catalysts, which utilize a coordination- or insertion-type mechanism during polymerization. In general, a Ziegler–Natta catalyst is a bimetallic coordination complex of a metal cation from groups I–III in the periodic table, such as triethyl aluminum, Al(C₂H₅)₃, and a transition metal compound from groups IV–VIII, such as titanium tetrachloride (TiCl₄). As an example, linear (i.e., high-density) polyethylene can be prepared by bubbling ethylene into a suspension of Al(C₂H₅)₃ and TiCl₄ in hexane at room temperature. Polypropylene of nearly 90% isotacticity can be prepared by the polymerization of propylene in the presence of titanium trichloride (TiCl₃) and diethylaluminum chloride, Al(C₂H₅)₂Cl, at 50°C. Similar catalyst systems can be used to polymerize other α -olefins such as 1-butene (H₂C=CH—CH₂—CH₃), geometric isomers of diolefins (e.g., isoprene), and even acetylene (HC≡CH).

Although the exact mechanism of coordination polymerization is still unclear, it is believed that the growing polymer chain is bound to the metal atom of the catalyst and that monomer insertion involves a coordination of the monomer with the metal atom. It is this coordination of the monomer that results in the stereospecificity of the polymerization. An illustration of the Cossee⁸ mechanism for the polymerization of propylene is illustrated in Figure 2-6. Coordination polymerizations can be terminated (poisoned) by introduction of water, hydrogen, aromatic alcohol, or certain metals such as zinc.

First-generation heterogeneous Z–N catalysts (e.g., TiCl₃/Al[C₂H₅)₂Cl]) for propylene polymerization achieved high isotacticity (ca. 90%) but low yield (e.g., 5 kg *i*-PP per g of Ti). Second-generation catalysts incorporating a Lewis base improved both catalyst activity and stereospecificity. Unfortunately, a problem with these catalyst systems was contamination of the *i*-PP with inactive Ti salts. More recent Z–N catalysts consist of TiCl₄ supported on MgCl₂, a trialkyl aluminum cocatalyst, and one or two Lewis bases as electron donors.

These third-generation catalysts achieve up to 98% isotacticity with high catalyst performance (>2400 kg PP/g Ti) which eliminates the need for catalyst removal.

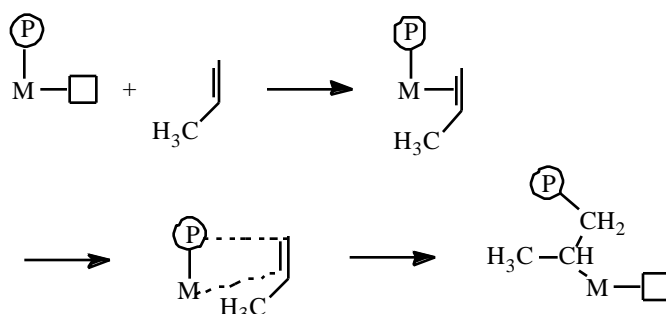


Figure 2-6 Proposed mechanism of monomer insertion during the Ziegler–Natta polymerization of propylene (after Cossee⁸). The small box represents a vacant coordination site on an octahedrally coordinated transition metal ion (M) that can coordinate with the π -bond of propylene. The symbol P represents the growing polypropylene chain.

Metallocene Polymerizations. In 1980, Sinn and Kaminsky⁹ reported a significant advance in the stereoregular homogeneous polymerization of ethylene, α -olefins including propylene, and several other commercially important monomers including styrene and methyl methacrylate. This new type of coordination polymerization uses metallocene catalysts.[†] Several different transition (typically from Group IVb) metals have been used in the preparation of metallocene catalysts including zirconium (i.e., zirconocene), titanium (i.e., titanocene), and hafnium (i.e., hafnocene). The order of metallocene activity is generally $Zr > Hf > Ti$. Metallocenes can be used to obtain extremely uniform polymers with narrow-molecular-weight distribution. Ethylene was the first olefin to be polymerized using metallocene catalysts. Metallocenes also can be used to copolymerize ethylene with propylene, butene, hexene, and octene. Compared with Z–N catalysts, metallocenes are more expensive but can be more productive in terms of the amount of polymer produced per quantity of catalyst.

Commercial metallocene polymers, with properties ranging from crystalline to elastomeric, were first produced in 1991 and are rapidly capturing the polyolefin market. The enhanced properties of some metallocene-catalyzed polymers open new opportunities for traditional commodity thermoplastics. For example, superior optical clarity, low-temperature ductility, and reduced amounts of impurities (e.g., catalyst metal residues) afford opportunities in the medical area. Utilizing metallocene chemistry, nearly 100% syndiotactic polypropylene (*s*-PP) (see Section 9.1.1) and syndiotactic polystyrene (*s*-PS) (see Section 9.1.2) have been produced for the first time on a commercial scale.

[†] The term metallocene was coined in the early 1950s to describe dicyclopentadienyliron (Cp_2Fe) ferrocene.

Metallocene catalysts are used with a co-catalyst typically methylaluminoxane (MAO), a complex mixture of methylaluminum oxide oligomers ($-\text{CH}_2\text{AlO}-$). MAO is formed by the controlled hydrolysis of trimethylaluminum. The catalytic activity of metallocene catalysts is directly proportional to the degree of oligomerization of the aluminoxane. Other Lewis acid co-catalysts like tetraphenylborates can be used to polymerize monomers containing substituent groups, such as methyl methacrylate.

The majority of Ziegler–Natta polymerization production units are designed for heterogeneous catalysis. To utilize existing facilities, metallocenes can be supported on a number of inorganic oxides such as SiO_2 (silica gel), Al_2O_3 , and MgCl_2 with or without MAO. For example, silica-supported metallocenes can be used to obtain LLDPE using the UNIPOL gas-phase process (see Section 2.3.5).

The most widely used metallocene catalysts consist of two (bent) cyclopentadienyl ligands (Cp_2MX_2) such as illustrated in Figure 2-7A. Many other metallocene structures are possible including a single cyclopentadienyl ring (Figure 2-7B) used in polymerization of *s*-PS. The cyclopentadienyl ring of a metallocene is singly bonded to the central metal atom by a σ -bond. A proposed mechanism of active site generation due to mixing of a bent metallocene with excess MAO in a solvent is shown in Figure 2-8.

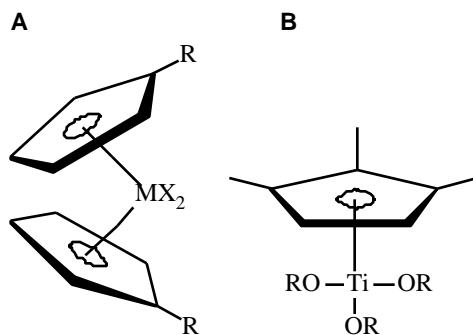


Figure 2-7 **A.** Typical metallocene catalyst for olefin polymerization (e.g., LLDPE, HDPE, *a*-PP, and ethylene–cycloalkene copolymer). The symbol M represents a transition metal (e.g., Ti, Hf, or Zr), R represents hydrogen or an alkyl group, and X represents a halogen (typically Cl or Br). **B.** single cyclopentadienyl ligand for *s*-PS.

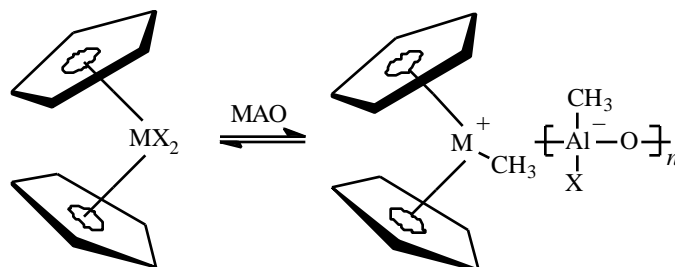


Figure 2-8 Proposed mechanism of active site generation in metallocene polymerization.

2.3 POLYMERIZATION TECHNIQUES

2.3.1 Bulk Polymerization

The simplest technique, and the one that gives the highest-purity polymer, is bulk polymerization. Only monomer, a monomer-soluble initiator, and perhaps a chain-transfer agent to control molecular weight are used. Advantages of this technique include high yield per reactor volume, easy polymer recovery, and the option of casting the polymerization mixture into final product form (i.e., cast polymerization). Among the limitations of bulk polymerization are the difficulty of removing residual traces of monomer and the problem of dissipating heat produced during the polymerization. Free-radical polymerizations are highly exothermic (typically 42 to 88 kJ mol⁻¹, see Table 2-5 for some examples), while the thermal conductivity of organic monomers and polymers are low as shown by values given in Table 2-8. An increase in temperature will increase the polymerization rate and, therefore, generate additional heat to dissipate. Heat removal becomes particularly difficult near the end of the polymerization when viscosity is high. This is because high viscosity limits the diffusion of long-chain radicals required for termination. This means that radical concentration will increase and, therefore, the rate of polymerization also will increase, as indicated by eq. 2.16. By comparison, the diffusion of small monomer molecules to the propagation sites is less restricted. This means that the termination rate decreases more rapidly than the propagation rate, and the overall polymerization rate, therefore, increases with accompanying additional heat production. This autoacceleration process has been called the Norrish–Smith,¹⁰ Trommsdorff,¹¹ or gel effect. In practice, heat dissipation during bulk polymerization can be improved by providing special baffles for improved heat transfer or by performing the bulk polymerization in separate steps of low-to-moderate conversion.

Table 2-8 Heat Capacity and Thermal Conductivity at 298 K

Material	C_p kJ mol ⁻¹ K ⁻¹	λ^* J m ⁻¹ s ⁻¹ K ⁻¹
Water	0.075	0.607
Benzene	0.136	0.141
Toluene	0.157	0.131
Styrene	0.182	0.137
Polystyrene	0.127	0.142
Poly(methyl methacrylate)	0.137	0.193
Poly(vinyl chloride)	0.059	0.168

$$* q = -\lambda(dT/dz).$$

Bulk-polymerization processes can be used for many free-radical polymerizations and some step-growth (condensation) polymerization. Important examples of polymers usually polymerized by free-radical bulk polymerization include polystyrene and poly(methyl methacrylate) for which cast polymerization accounts for about half of the total production. Low-density (i.e., high-pressure) polyethylene and some ethylene copolymers are sometimes produced by bulk free-radical polymerizations.

2.3.2 Solution Polymerization

Heat removal during polymerization can be facilitated by conducting the polymerization in an organic solvent or preferably water which has both cost and handling advantages as well as high thermal conductivity (Table 2-8). The requirements for selection of the solvent are that both the initiator and monomer be soluble in it and that the solvent have acceptable chain-transfer characteristics and suitable melting and boiling points for the conditions of the polymerization and any subsequent solvent-removal step. Solvent choice may be influenced by other factors such as flash point, cost, and toxicity. Examples of suitable organic solvents include aliphatic and aromatic hydrocarbons, esters, ethers, and alcohols. Often, the polymerization can be conducted under conditions of solvent reflux to maximize heat removal. Reactors are usually stainless steel or glass lined. The obvious disadvantages of solution polymerization are the small yield per reactor volume and the requirement for a separate solvent-recovery step.

Many free-radical and ionic polymerizations are conducted in solution. Important water-soluble polymers that can be synthesized in aqueous solution include poly(acrylic acid), polyacrylamide, poly(vinyl alcohol), and poly(*N*-vinylpyrrolidinone). Poly(methyl methacrylate), polystyrene, polybutadiene, poly(vinyl chloride), and poly(vinylidene fluoride) can be polymerized in organic solvents.

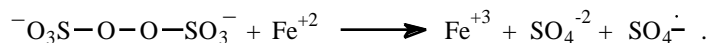
2.3.3 Suspension Polymerization

Improved heat transfer can also be obtained by utilizing the high thermal conductivity of water through either suspension or emulsion polymerization. In suspension ("bead" or "pearl") polymerization, a batch reactor fitted with a mechanical agitator is charged with a water-insoluble monomer and initiator. Sometimes, a chain-transfer agent may be added to control molecular weight in a free-radical polymerization. Droplets of monomer containing the initiator and chain-transfer agent are formed. These are typically between 50 and 200 μm in diameter and serve as miniature reactors for the polymerization. Coalescence of these "sticky" droplets is prevented by the addition of a protective colloid, typically poly(vinyl alcohol), and by constant agitation of the polymerization mixture. Near the end of the polymerization, the particles harden and can then be recovered by filtration, which is followed by a final washing step. Although solvent cost and recovery operations are minimal in comparison with solution polymerization, polymer purity is low due to the presence of suspending and other stabilizing additives that are difficult to completely remove. In addition, reactor capital costs are typically higher than for solution polymerization. Polymers commonly produced by free-radical suspension polymerization include styrenic ion-exchange resins (Section 2.4.1), extrusion and injection-molding grades of poly(vinyl chloride), poly(styrene-co-acrylonitrile) (SAN), and extrusion-grade poly(vinylidene chloride-co-vinyl chloride).

2.3.4 Emulsion Polymerization

Another technique that utilizes water as a heat-transfer agent is emulsion polymerization. In addition to water and monomer, a typical reactor-charge for an emulsion polymerization consists of a *water-soluble* initiator, a chain-transfer agent, and a surfactant such as the sodium salt of a long-chain fatty acid. The (hydrophobic) monomer molecules form large droplets. These are stabilized by the surfactant molecules whose hydrophilic ends point outward and whose hydrophobic (aliphatic) ends point inward toward the monomer droplet, as illustrated in Figure 2.9. The size of monomer droplets depends upon the polymerization temperature and the rate of agitation. Above a certain surfactant concentration, the *critical micelle concentration*, residual surfactant molecules can align to form *micelles*. Depending upon the nature of the surfactant, the micelles are small rod-like or spherical structures ($\sim 50 \text{ \AA}$ in length) that contain between 50 and 100 surfactant molecules. Surfactants prepared from long-chain fatty acids favor the formation of rod-like micelles.

As indicated above, an important difference between suspension and emulsion polymerization is that the initiator used in an emulsion polymerization must be soluble in water. An example of a commonly-used water-soluble initiator is the persulfate-ferrous (K_2SO_4) *redox* initiator,¹² which yields a radical sulfate anion through the reaction



Nea- ambient temperature and a neutral pH typically favor K_2SO_4 -initiated emulsion polymerization.

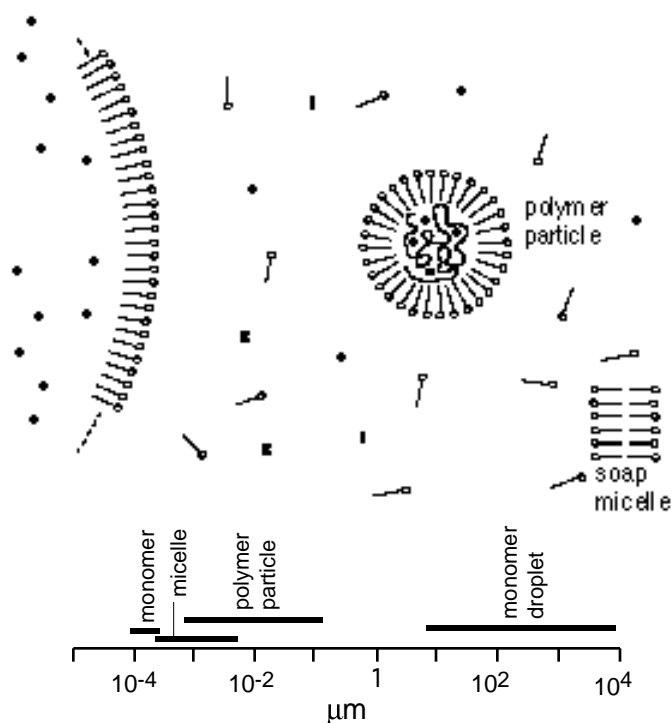


Figure 2-9 Representation of the composition of an emulsion polymerization and relative particle size. Symbols: \bullet , monomer molecule; I, initiator molecule; and R, primary radical. (Adapted from P. Rempp and E. W. Merrill, *Polymer Synthesis*, Wiley-VCH, Weinheim, Germany, 1986, with permission of the publisher.)

During the emulsion-polymerization process, monomer molecules that have a small but significant water solubility can migrate from the monomer droplets through the water medium to the center of the micelles. Polymerization is initiated when the water-soluble initiating radical enters a monomer-containing micelle. Due to the very high concentration of micelles, typically 10^{18} per mL, compared to that of the monomer droplets (10^{10} to 10^{11} per mL), the initiator is statistically more likely to enter a micelle than a monomer droplet. As the polymerization proceeds, additional monomer molecules are transferred from the droplets to the growing micelles. At 50% to 80% monomer conversion, the monomer droplets are depleted and the swollen micelles are transformed to relatively large polymer particles, typically between 0.05 and 0.2 μm in diameter. The suspension of polymer particles in water is

called a *latex*. The latex is very stable and can be used as is (e.g., latex paints) or the polymer can be recovered by coagulation of the latex with acids or salts.

The free-radical kinetics of emulsion polymerization is different from the usual free-radical kinetics of bulk, solution, or suspension polymerization as described in Section 2.2.1. Smith and Ewart¹³ have analyzed the kinetics of free-radical emulsion polymerization. They assumed that the monomer-swollen micelles are sufficiently small that, on the average, only *one* propagating chain or *one* terminated chain can exist inside a particle at any time. This means that the radical concentration, $[M_x^\bullet]$, is simply equal to one-half of the particle concentration, N (units of particle number per mL), which in turn is determined by the surfactant and initiator concentrations, among other factors. Therefore, the polymerization rate (see eq. 2.16) is given as

$$R_p = k_p (N / 2)[M] \quad (2.47)$$

where $[M]$ is the concentration of monomer inside the swollen polymer particles. This expression should be compared to the usual steady-state rate expression for free-radical polymerization given by eq. 2.23. While both rates are proportional to monomer concentration, the rate of emulsion polymerization is no longer proportional to the square root of initiator concentration but follows a more complicated dependence on initiator concentration through its dependence on N .

When the monomer is hydrophilic, emulsion polymerization may proceed through an *inverse emulsion* process. In this case, the monomer (usually in aqueous solution) is dispersed in an organic solvent using a water-in-oil emulsifier. The initiator may be soluble in either the water or oil phase. The final product in an inverse emulsion polymerization is a colloidal dispersion of a water-swollen polymer in the organic phase.

2.3.5 Solid-State, Gas-Phase, and Plasma Polymerization

In addition to the usual methods of polymerization such as bulk and solution, polymers can be prepared in the gas or vapor phase. This is especially the case for the polymerization of olefins such as ethylene. In the Unipol process for PE, which is illustrated in Figure 2-10, gaseous ethylene and solid catalyst (chromium or other complexes) are combined in a continuous fluidized-bed reactor. Since the polymerization is highly exothermic, proper management of heat transfer is critical to prevent agglomeration of the particles and a shutdown of the process. Variations of this process, which accounts for over 50% of the world's licenses for polyethylene production, have been used for the polymerization of propylene and the copolymerization of ethylene and propylene. A new generation Unipol II process produces LLDPE for film application.¹⁴

Solid-State Polymerization. In addition to gas-phase polymerizations, more exotic routes may be followed for specialty applications. For example, some monomers in their crystalline state can be polymerized by heating or by irradiation (visible, x-ray, UV, or

γ -radiation) to give extended-chain polymers oriented along crystallographic directions. The result is a polymer single-crystal with interesting optical properties. As an example, crystalline polyoxymethylene can be obtained by the γ -irradiation of trioxane or tetraoxane crystals.

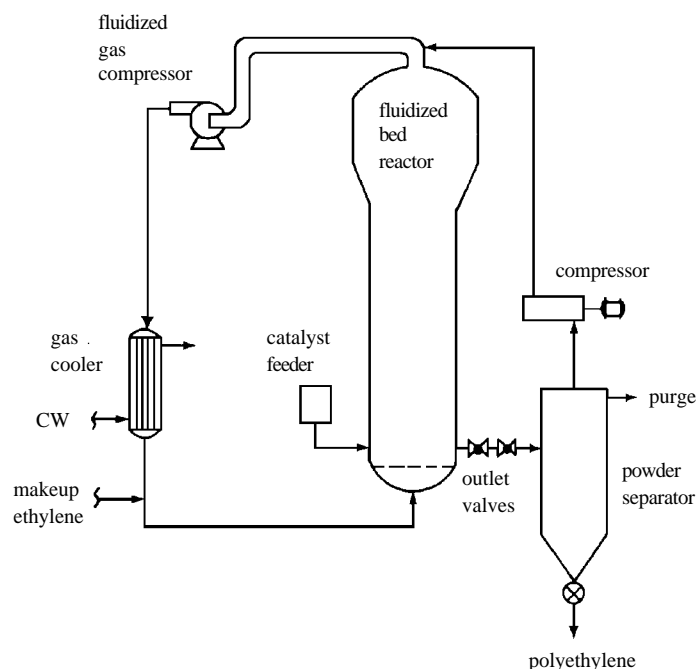


Figure 2-10 Unipol process for the polymerization of ethylene. (Adapted from N. F. Brockmeier, in the *Concise Encyclopedia of Polymer Science and Engineering*, J. I. Kroschwitz, ed. Copyright ©1990 by John Wiley & Sons. This material is used by permission of John Wiley & Sons, Inc.)

Plasma Polymerization. A wide variety of monomers can also be polymerized in a plasma environment consisting of a low-pressure glow discharge of positively and negatively charged species, electrons, excited and neutral species, and electromagnetic radiation. Plasma polymerization can be used to prepare graft copolymers or to deposit a thin polymer film on a metal or other substrate (e.g., a photoresist on a silicon wafer or a corrosion-resistant coating on a metal). Dense, uniform films of polyfuran and polythiophene can be prepared by plasma polymerization to prepare polymer waveguides. Plasma activation can be used to modify surface properties such as wettability, adhesion, and biocompatibility. For example, catheters can be plasma modified with heparin to prevent blood clotting. Plasma treatment also can be used to remove contamination from the surface of composite fibers to improve adhesion to the matrix. Plasma-polymerized films can be extremely uniform but are

typically strongly crosslinked. For this reason, Electron Spectroscopy for Chemical Analysis (ESCA) and static Secondary Ion Mass Spectroscopy (SIMS) are the primary methods used to characterize plasma-modified surfaces. These techniques provide significant information about the elemental and chemical composition of the film including the presence of functional groups on the surface.

The preferred method for plasma polymerization is by the injection of an organic precursor into a flowing afterglow reactor as illustrated in Figure 2-11. In this scheme, a large flow of argon gas passes between two aluminum electrodes. The argon is excited by the generation of radio frequency (RF) energy between the electrodes. The RF energy dissociates the gas into electrons, ions, free radicals, and metastable excited species. A flow of an organic precursor is added through a small diameter tube. The excited species formed in the afterglow where the precursor is introduced reacts with the surface of the substrate.

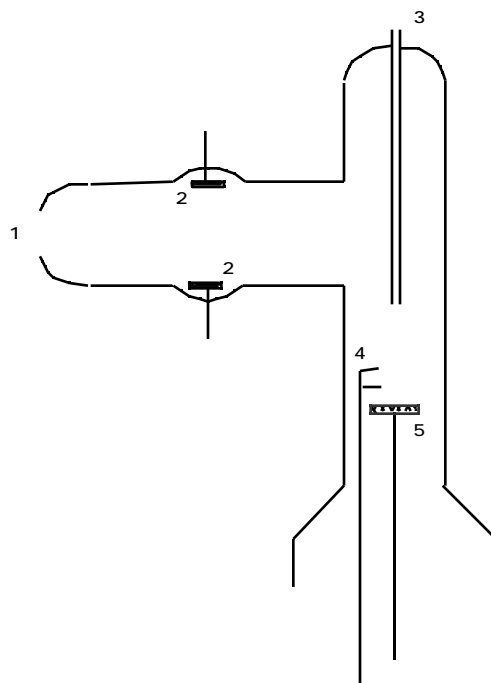


Figure 2-11 Schematic representation of a flowing afterglow plasma reactor. 1. Argon inlet. 2. Al electrodes. 3. Organic precursor reentrant tube. 4. Langmuir probe used to measure plasma density. 5. Quartz microbalance or substrate. (Adapted from *Trends in Polymer Science*, Vol 1, pp 40–45, P. D. Haaland and S. J. Clarson, "Plasma and Polymers: Synthesis Under Extreme Conditions", Copyright 1993, with permission from Elsevier Science.)

2.3.6 Polymerization in Supercritical Fluids

A supercritical fluid (SCF) is defined as one that is above its critical temperature (T_c) and critical pressure (p_c). Supercritical fluids combine the properties of both gases and liquids such as high diffusivity, low viscosity, and liquid-like densities. Supercritical fluids also show unusual dissolving power (e.g., supercritical water can dissolve oil). Solvent strength can be adjusted through control of pressure, temperature, or both. Analytical applications include decaffeination of coffee, desulfurization of coal, pulp processing, and chemical extraction. Other potential applications include plastic recycling, fiber spinning, and drug impregnation.

Critical properties of water, carbon dioxide, and several organic compounds are listed in Table 2-9. As shown, critical properties vary widely. For analytical and commercial extraction processes, carbon dioxide is the most commonly used supercritical fluid due to its low critical temperature (31°C) and pressure (73 atm), low cost, low toxicity, and ease of disposal. For example, supercritical CO₂ is used as an alternative to the use of chlorinated solvents for the decaffeination of coffee. By comparison, water has very high critical properties ($T_c = 374^\circ\text{C}$, $p_c = 218$ atm); however, the properties of supercritical water are such that it has received attention as a means to destroy hazardous wastes.

Table 2-9 Critical Properties of Important Supercritical Fluids

Compound	T_c (°C)	p_c (atm)
Methane	-82.1	45.8
Ethane	32.2	48.2
Carbon Dioxide	31.0	72.9
<i>n</i> -Butane	152.0	38.2
Toluene	320.8	41.6
Water	374.1	218.3

Recently, a number of monomers have been polymerized in SCFs. The propagation rate of free-radical polymerization increases with increasing pressure and, therefore, high-molecular-weight polymers can be obtained by using SCFs. Advantages of supercritical fluids include the adjustment of the precipitation threshold and the minimization of swelling of the precipitate. Examples of the use of SCFs include the free-radical polymerization of styrene, vinyl acetate, acrylonitrile, and methyl methacrylate. Initiators consist of typical free-radical initiators including AIBN and *t*-butyl peroxide (see Section 2.2.1). A particular advantage of supercritical fluids lies in the polymerization of fluoropolymers for which supercritical CO₂ can be used in place of chlorofluorocarbons (see Section 2.5.1). Supercritical CO₂ also can be used for cationic and ring-opening metathesis reactions.

2.4 REACTIONS OF SYNTHETIC POLYMERS

In many cases a polymer can be chemically modified to improve some property, such as biocompatibility, fire retardancy, or adhesion, or to provide specific functional groups for ion-exchange or other applications. For example, bromination is sometimes used to impart fire retardancy to some polymers. As another example, poly(vinyl chloride) can be chlorinated after polymerization to increase its softening temperature or to improve its ability to blend with other polymers. In some cases, important commercial polymers can be produced only by the chemical modification of a precursor polymer. Examples include poly(vinyl alcohol), poly(vinyl butyral), cellulose derivatives such as cellulose acetate and cellulose nitrate, and polyphosphazenes—an interesting group of inorganic polymers.

2.4.1 Chemical Modification

Chloromethylation. Chloromethylation of polystyrene (see Figure 2-12), by reacting with a chloromethyl ether in the presence of a Friedel-Crafts catalyst like aluminum chloride, AlCl_3 , can be used to introduce functionality such as aldehyde or carboxylic acid groups in polystyrene. Aldehydes serve to form a Schiff base with protein amines. In the Merrifield synthesis of proteins, crosslinked polystyrene (PS) beads that have been lightly chloromethylated provide the anchor sites for the sequential addition of amino acids. Highly chloromethylated PS can be quaternized with tertiary amines to yield water-soluble polymers, ionomers, and ion-exchange resins, as described in the following section. Chloromethylated PS also can be reacted with a phosphide to introduce phosphinic ligands for binding metal coordination complexes in the preparation of polymer-bound catalysts.

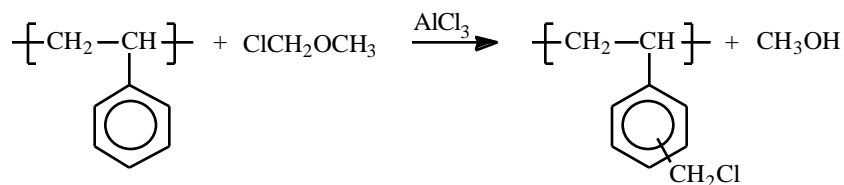


Figure 2-12 Chloromethylation of polystyrene.

Surface Modification. In many cases it may be desirable to modify the surface of a polymer to provide sites for immobilization of enzymes or other biopolymers or to improve the solvent resistance or biocompatibility of a polymer. As mentioned earlier (Section 2.3.5), plasma activation is one approach to modify polymer surfaces. Another method is direct fluorination, oxidation, nitration, and sulfonation. For example, the surface of a hydrocarbon polymer such as polyethylene or polypropylene can be fluorinated by exposure to 5% to 10% fluorine gas diluted in nitrogen for one to 15 minutes. The fluorinated surface pro-

vides hydrophobicity, oxidation resistance, and solvent resistance for applications such as plastic fuel tanks and rubber gloves.

Ion-Exchange Resins. Another need for chemical modification is the preparation of ion-exchange resins. Cation-exchange resins possess a fixed negative charge and exchange cations such as Ca^{2+} , Na^+ , and H^+ . Anion-exchange resins possess a positive charge on the functional group or are positively charged during the ion-exchange reaction during which anions such as HCO_3^- , SO_4^- , and OH^- are exchanged. Most ion-exchange resins are prepared by suspension polymerization of monomers such as styrene, which can be crosslinked by incorporation of a few percent of a difunctional comonomer such as divinylbenzene. The resulting beads are macroporous and can be used as a column packing. Functionalization can be obtained by different chemical routes, such as sulfonation, phosphonation, phosphination, chloromethylation, amino-methylation, aminolysis, and hydrolysis. For example, a cation-exchange resin can be prepared by sulfonation of a crosslinked polystyrene bead in concentrated sulfuric acid or in a molecular complex of SO_3 with an organic solvent, such as dioxane. Sulfonation primarily occurs at the *para*-position with some *ortho*-substitution. A styrenic anion-exchange resin can be prepared by reacting the benzyl chloride of chloromethylated polystyrene (see Figure 2-12) with a tertiary amine, $\text{N}(\text{CH}_3)_3$. Examples of styrenic ion-exchange resins are illustrated in Figure 2-13.

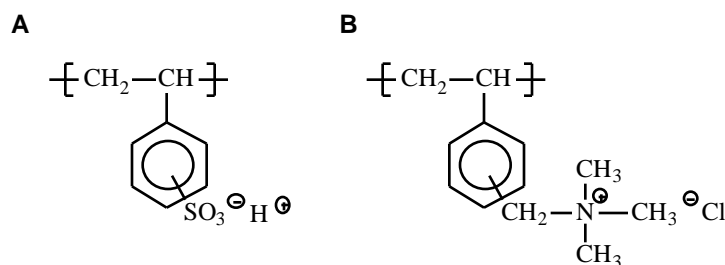


Figure 2-13 Example of a strongly acidic cation-exchange resin (**A**) and a strongly basic anion-exchange resin (**B**) prepared from polystyrene.

2.4.2 Preparation of Polymer Derivatives

Cellulose. Cellulose, which can be obtained from wood pulp and short fibers left from cotton recovery, is one of nature's most abundant biopolymers. A typical chain is composed of 2,000 to 6,000 anhydroglucose units (typical molecular weight of 300,000 to 1,000,000) each of which contains three hydroxyl groups and is linked by an acetal bridge, as shown in Figure 2-14. The rigid chain of cellulose is strongly hydrogen bonded and highly crystalline. For these reasons, cellulose is essentially insoluble and infusible (degrades before melting), and therefore fibers and films can be obtained only by chemically modifying cellulose. As

will be described in Section 8.2.2, cellulose fiber (rayon) or film (cellophane) can be obtained by the *viscose* process. In this regeneration process, cellulose pulp is first reacted with carbon disulfide to form cellulose xanthate, which is soluble in a caustic solution. Cellulose xanthate is then converted back to cellulose (regeneration) by treatment with aqueous sulfuric acid.

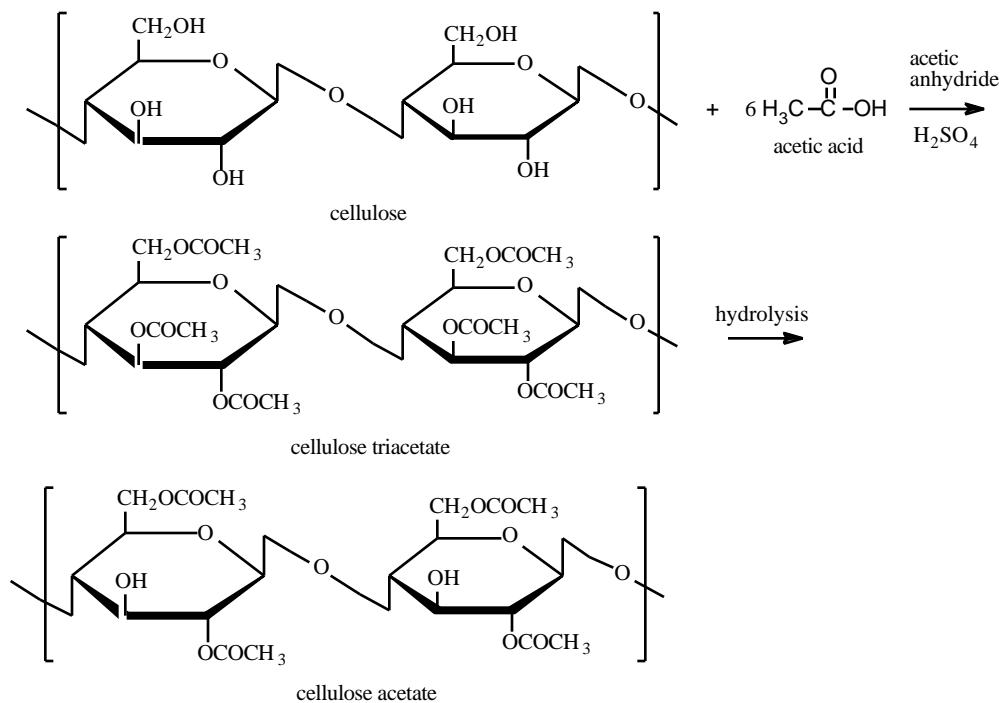
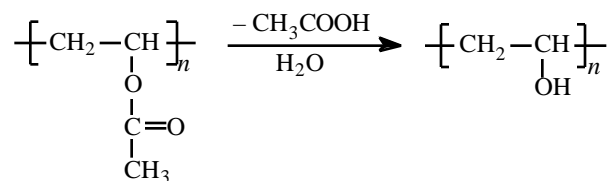


Figure 2-14 Preparation of cellulose acetate from cellulose. For simplicity, lone hydrogen atoms on the cellulose repeating units are omitted.

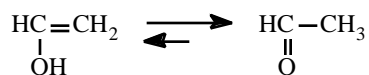
Various soluble cellulose derivatives can be obtained by chemical modification of the hydroxyl groups. One of the most important of these is cellulose acetate, which is obtained by reacting cellulose with glacial acetic acid in the presence of acetic anhydride and traces of sulfuric acid in refluxing methylene chloride (Figure 2-14). If all the hydroxyl groups are reacted, the polymer is known as cellulose triacetate (CTA), which can be wet spun into fiber (acetate) from a methylene chloride–alcohol solvent mixture. Cellulose triacetate can be partially hydrolyzed to give cellulose diacetate in which two (secondary) of the three hydroxyl groups in each anhydroglucose unit remain acetylated. In commercial grades of cellulose acetate, about 65% to 75% of all available hydroxyl groups remain acetylated. This polymer is

amorphous and highly soluble in many solvents including acetone, from which it can be dry spun (see Section 8.2.4).

Poly(vinyl alcohol) and Poly(vinyl butyral). Poly(vinyl alcohol) (PVAL) is obtained by the direct hydrolysis (or catalyzed alcoholysis) of poly(vinyl acetate) (PVAC) as shown by the following reaction:



Poly(vinyl acetate) is produced by free-radical emulsion or suspension polymerization. It has a low glass-transition temperature (ca. 29°C) and finds some applications as an adhesive. Poly(vinyl alcohol), which is used as a stabilizing agent in emulsion polymerizations and as a thickening and gelling agent, cannot be polymerized directly because its monomer, vinyl alcohol, is isomeric with acetaldehyde



where the equilibrium is biased towards the ketone structure.

Another important polymer, poly(vinyl butyral) (PVB), which is used as the film between the layers of glass in safety windshields, is obtained by partially reacting PVAL with butyraldehyde, as shown in Figure 2-15. For safety-glass applications, approximately 25% of the repeating units of PVAL are left unreacted to promote adhesion to the glass through interaction of the hydroxyl group with the surface (i.e., silanol) groups of the glass.

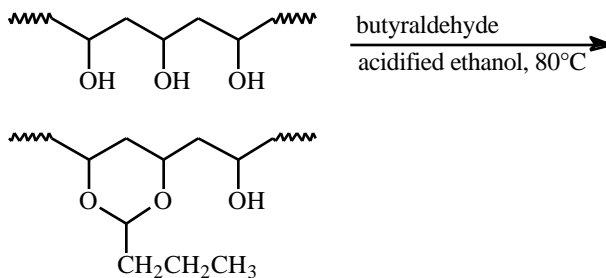
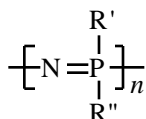


Figure 2-15 Production of poly(vinyl butyral) from a poly(vinyl alcohol) precursor.

Poly(organophosphazenes). Another class of polymers that are obtained by chemical modification of a precursor polymer includes a wide variety of poly(organophosphazenes).¹⁶ These are inorganic polymers having alternating nitrogen–phosphorus backbone, as follows:



A very large number of different substituent groups (R', R'') can be linked to the phosphorus atom. These include alkoxy, aryloxy, amino, alkyl, aryl, or even an inorganic or organometallic unit. At present, more than 300 different poly(organophosphazenes) have been prepared. Properties vary from elastomeric (T_g -80°C) to microcrystalline. Potential applications of poly(organophosphazenes) include those in which good chemical stability is required, such as O-rings, gaskets, and fuel lines, and in areas where good biostability and biocompatibility are necessary, such as in the encapsulation of pancreatic cells. Poly(organophosphazenes) also exhibit extremely high permeability for fixed gases and organic liquids and may find use in membrane applications (see Section 12.1).

The precursor polymer for all poly(organophosphazenes) is poly(dichlorophosphazene), which is obtained from the radiation- or plasma-polymerization (see Section 2.3.5) of hexachlorocyclotriphosphazene. Poly(dichlorophosphazene) is unstable due to its high susceptibility to hydrolysis, producing phosphoric acid, hydrogen chloride, and ammonia as by-products. Fortunately, the active chlorine sites are readily substituted by nucleophiles such as alkoxides, aryloxides, and amines to yield a wide variety of high-molecular-weight poly(organophosphazenes) that are chemically and thermally stable. These common substitution reactions are illustrated in Figure 2-16.

2.5 SPECIAL TOPICS IN POLYMER SYNTHESIS

Sections 2.1 and 2.2 described the traditional step-growth and chain-growth polymerization methods that have been developed over the past 75 years and are widely used in today's commercial plastics industry. During the past few years there has been renewed interest in several specialized polymerization methods as well as the development of new approaches. These range from metathesis ring-opening polymerization, first developed in the early 1960s, the use of macromers for the preparation of graft copolymers, and group-transfer polymerization, to more recent techniques such as atom-transfer radical polymerization and genetic engineering.

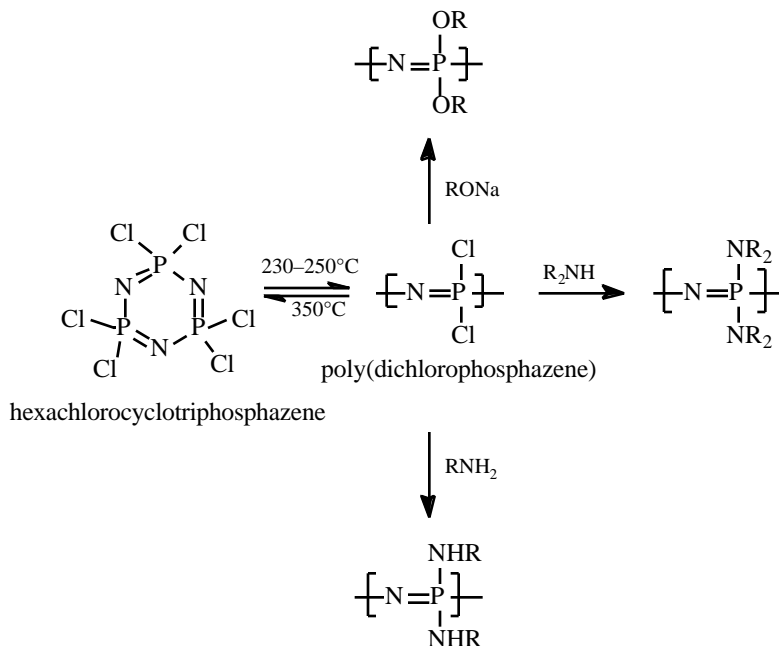


Figure 2-16 Ring-opening polymerization of hexachlorocyclotriphosphazene to poly(dichlorophosphazene) and representative substitution reactions to prepare different poly(organophosphazenes).

2.5.1 Metathesis

Cyclic olefins, like cyclobutene and cyclopentene, can undergo a ring-opening polymerization called *metathesis* to yield elastomers (polyalkenamers) having attractive properties for specialty applications. Polyalkenamers obtained from the metathesis polymerization of cyclooctene and norbornene (bicyclo[2.2.1]hept-2-ene) are specialty elastomers. Polymerizations proceed with good rates at room temperature, and polymer stereochemistry can be controlled by the choice of catalyst. Typical catalysts for olefin metathesis include Ziegler types such as prepared from the reaction product of tungsten hexachloride with ethanol and ethyl–aluminum dichloride, $WCl_6/(C_2H_5)_3Al$. Other important examples of catalysts include MoO_3/Al_2O_3 and $TiCl_4/LiAlR_4$. As an example, routes in the production of *cis*- and *trans*-isomers of polypentenamer by the metathesis polymerization of cyclopentene are illustrated in Figure 2-17. The unsaturated site of the polypentenamer is available for subsequent functionalization reactions.

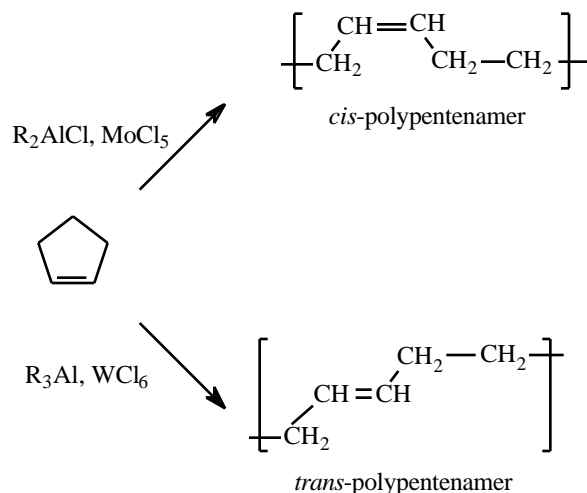


Figure 2-17 Ring-opening metathesis of cyclopentene.

The mechanism of metathesis polymerization is a typical coordination type involving the propagation of a metal-carbene complex via a metallacyclobutane intermediate, as illustrated in Figure 2-18. Metathesis polymerization of highly strained cycloalkanes such as norbornene and cyclobutene proceed much more rapidly than less strained structures such as cyclopentene (Figure 2-17).

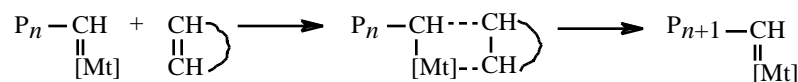


Figure 2-18 A propagation step in the metathesis polymerization of a cycloalkene where P represents a repeat unit, n is the degree of polymerization, and Mt represents a metal complex.

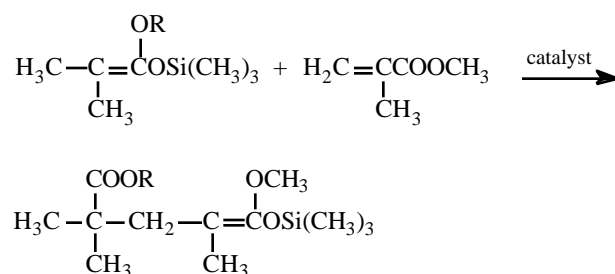
2.5.2 Group-Transfer Polymerization

Group-transfer polymerization (GTP), developed by DuPont in 1983,¹⁷ is the "living" polymerization of α,β -unsaturated esters (principally acrylates and methacrylates), ketones, nitriles, or amides with initiation by silyl ketene acetals. Examples of monomers that can be polymerized in this manner include methyl methacrylate, ethyl acrylate, butyl acrylate, and 2-methacryloxyethyl acrylate. Typical initiators are 1-alkoxy-1-(trimethylsiloxy)-2-methyl-1-alkenes such as 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene used in the polymerization of methyl methacrylate. The initiator is activated by nucleophilic catalysts such as

soluble fluorides, bifluorides [e.g., tris(dimethylamino)sulfonium bifluoride], azides, and cyanides.

During the polymerization, the reactive ketene silyl acetal group is transferred to the head of each new monomer molecule as it adds to the chain, hence the name group-transfer polymerization. As in anionic polymerization, the ratio of monomer to initiator concentration determines the molecular weight. An important example is the GTP of methyl methacrylate shown in Figure 2-19.

A



B

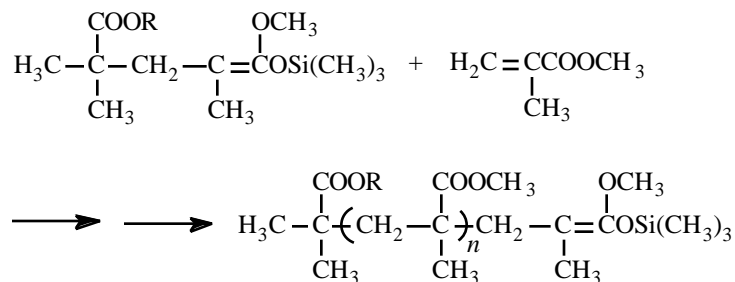


Figure 2.19 Group-transfer polymerization of methyl methacrylate. **A.** Initiation of monomer. **B.** Propagation.

Group-transfer polymerizations are typically conducted in a solution using an organic solvent such as toluene and THF at low temperatures (ca. 0° to 50°C). Active hydrogen compounds like some protonic solvents will stop the polymerization. For this reason, the polymerization environment must be completely free of water. Under these conditions, the polymerization will proceed until all monomer is exhausted as in other "living" polymerizations; however, high-molecular-weight polymers with molecular weights in excess of 100,000 are difficult to achieve unless the monomer, solvent, initiator, and catalyst are extremely pure. The high cost of GTP relative to more traditional free-radical polymerizations and the use of toxic catalysts such as azides and cyanides have limited widespread commercial utilization. Potential applications include high-performance automotive finishes, the fabrication of silicon chips, and coatings for optical fibers.

2.5.3 Macromers in Polymer Synthesis

A macromer or macromonomer is an abbreviation of the term *macromolecular monomer*. As the name suggests, a macromer is a low-molecular-weight oligomer or polymer with a functional group (F) at the chain end. This functional group can further polymerize to yield a higher-molecular-weight polymer. Examples of functional moieties include a vinyl group as well as a variety of difunctional chemical groups such as a dicarboxylic acid, diol, or diamine that can be used in a step-growth (or condensation) polymerization step. One use for macromers is controlled graft copolymerization. In this case, suitable comonomer units are contained in a prepolymer. The macromer then attaches to the comonomer sites and forms branches, as illustrated in Figure 2-20. These graft copolymers can be used as compatibilizers for polymer blends (see Section 7.2) and as surface-modifying agents.

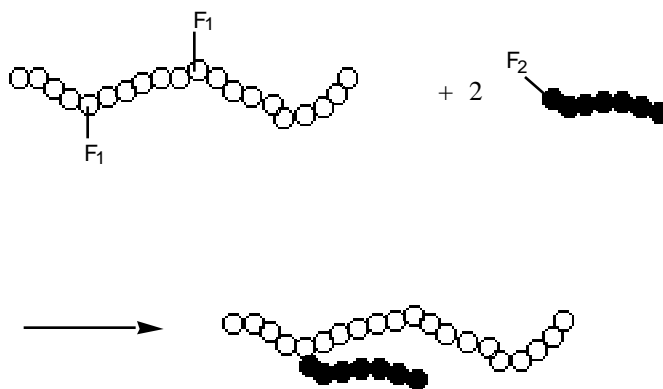


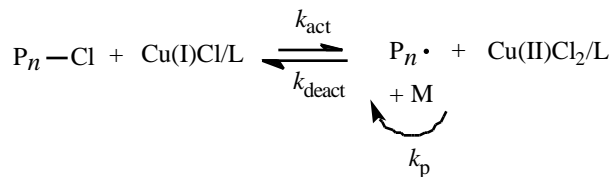
Figure 2-20 Graft polymerization by attachment of two macromers with functional group F₂ to a prepolymer with two complementary functional groups F₁.

2.5.4 Atom Transfer Radical Polymerization

Atom transfer radical addition, ATRA, is a tool for the formation of carbon–carbon bonds in organic synthesis. In 1995, Matyjaszewski and others^{18–20} adopted this approach to the polymerization of styrene and (meth)acrylates. This extension of ATRA to free radical polymerization is called atom transfer radical polymerization or simply ATRP. Polymers with high molecular weight (ca. 10^5) and a low polydispersity ($\bar{M}_w/\bar{M}_n < 1.3\text{--}1.5$) can be obtained by ATRP. This controlled/living free-radical polymerization also can be used to polymerize acrylonitrile and acrylamide and to prepare a variety of block copolymers, star polymers, and hyperbranched polymers.

The basic ingredients of an ATRP include a transition metal catalyst, M_t^n (Cu or Fe),* complexed by a ligand (L) compound (a halogen atom transfer promotor) and an organic halide, R-X (X = Br, Cl), which serves as the free-radical initiator. By using specialized initiators, ATRP can be used to obtain polymers with specific end-functional groups such as vinyl, hydroxyl, and cyano groups.²¹ A common example of a transition-metal halide used in ATRP is Cu(I)Cl. Common ligands include multidentate nitrogen compounds such as 2,2'-bipyridine (bpy), and 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy), and 1,10-phenanthroline (phen). An original recipe for the ATRP of styrene included 1-phenylethyl chloride (1-PECl), Cu(I)Cl, and bpy.¹⁸ More recently, ligands with reduced toxicity and cost, such as iminodiacetic acid (IDA) which complexes with Fe(II) and Fe(III), are being considered for ATRP.²²

Initially in ATRP, the transition metal complex, M_t^n/L , abstracts the halogen atom from the organic halide to form the oxidized species $X-M_t^{n+1}/L$ and the organic radical $R\cdot$. The radical can then add monomer, M, during a propagation step. The radical is rapidly deactivated by reacting with the oxidized transition metal halide complex to reform the initial transition metal complex and halogen-terminated chain, P_n-X , as illustrated below for the Cu(I)Cl redox equilibrium.



The living nature of ATRP is due to the fast equilibration between $P_n\cdot$ and the non-propagating halogen-terminated polymer (P_n-X). The equilibrium constant is

$$K_e = \frac{k_{act}}{k_{deact}} = \frac{[P_n\cdot][Cu(II)X_2]}{[P_n-X][Cu(I)X]} \quad (2.48)$$

A low equilibrium constant is required to maintain a low radical concentration, thereby reducing the potential of termination reactions. The number-average degree of polymerization in ATRP is determined by the ratio of initial monomer to organic halide initiator as

$$\bar{X}_n = \frac{[M]_o}{[RX]_o} \times \text{monomer conversion} \quad (2.49)$$

* The superscript n in M_t^n represents the oxidation state of the transition metal.

A very attractive feature of ATRP is that it combines the advantages of controlled molecular weight and low polydispersity offered by anionic living polymerization (see Section 2.2.2) with the ease of a free-radical polymerization. The requirement of achieving extremely pure polymerization conditions that limits the general applicability of anionic living polymerization is not an issue in ATRP.

2.5.5 Genetic Engineering

Naturally-occurring structural polymers such as collagen, silk, and elastin (see Section 8.1.1) contain repetitious short sequences of amino acids that contribute to their high tensile strength and resilience. Synthetic analogues of these polymers can be obtained by the synthesis of genes and their bacterial expression.^{23, 24} Such recombinant DNA methods offer opportunities to prepare polymers with precise control of molecular weight, stereochemistry, and monomer sequence. As illustrated in Figure 2-21, the first step is to encode the desired amino acid sequence into a complementary segment of double-stranded DNA obtained by solid-phase organic synthesis. Next, the synthetic gene is incorporated into a plasmid (a circular portion of a double-stranded DNA) obtained from the bacterium, *Escherichia coli*. The recombinant plasmid is then inserted into a strain of *E. coli* that can express the target protein.

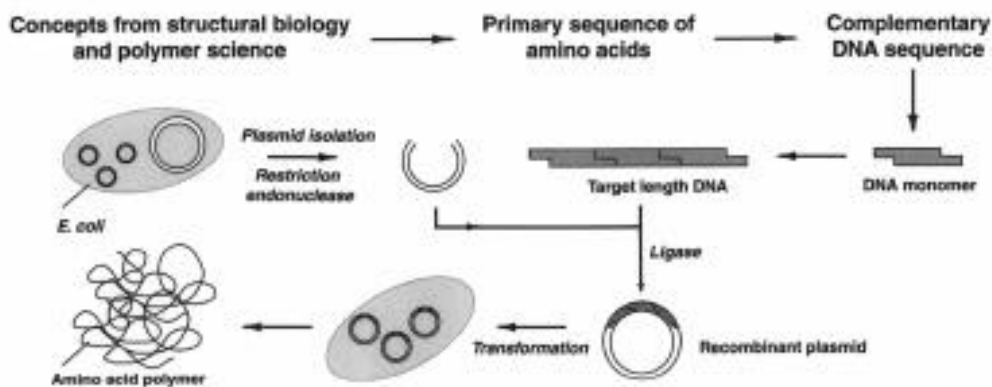


Figure 2-21 Steps in the genetic synthesis of new protein-like polymers. (Courtesy of D. Tirrell.)

Examples of genetically engineered protein-like polymers include elastin analogues capable of temperature- or pH-dependent dimensional changes. For example, poly(valine–proline–glycine–valine–glycine), crosslinked by γ -irradiation, will contract with an increase in temperature. Other examples include adhesive proteins, monodisperse liquid crystalline poly(γ -benzyl-L-glutamate), optically active poly(α ,L-glutamic acid), and other synthetic

structural proteins such as spider silk and collagen. Genetic engineering provides an opportunity for molecular design of new materials through substitution of any one of the 20 naturally occurring α -amino acids by the corresponding amino acid chemically modified for specific functionality. For example, interesting selenium arrays have been prepared by incorporating selenomethionine in place of methionine.²³

2.6 CHEMICAL STRUCTURE DETERMINATION

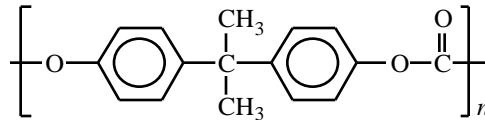
This chapter has described a variety of techniques used to synthesize polymers and copolymers. Once the polymer has been made, several analytical methods are available to confirm that the polymer made is actually the one desired and to identify various specific features of the polymer microstructure, such as comonomer composition and sequence, stereoregularity, branching, crystallinity, orientation, and oxidation sites if thermooxidative degradation has occurred (see Chapter 6). In addition, the presence of various additives, such as stabilizers and lubricating agents, or contaminants that may have been introduced during polymerization or in processing can be readily identified. The most important of these techniques include the common spectroscopic methods such as infrared, nuclear magnetic resonance (NMR), and Raman spectroscopy. Applications of spectroscopic methods to polymer characterization are briefly described in this section. In this, a general understanding of the basic principles of spectroscopy is assumed.

2.6.1 Vibrational Spectroscopy

Perhaps the most widely used method to characterize polymer structure is infrared spectroscopy, particularly Fourier transform infrared (FTIR) spectroscopy.²⁵ Polymer samples for IR analysis can have a variety of forms including thin film, solution, or a pellet containing a mixture of the granulated polymer and an IR-transparent powder such as potassium bromide. Bulk samples can be analyzed by reflection or attenuated total reflectance (ATR).

The IR spectra of a polymer is unique, and a large number of spectra libraries are available to assist identification.²⁶ Several atomic groups, such as $-\text{CH}$, $-\text{CO}$, and $-\text{CH}_3$, are readily identified by the presence of a single absorption band. As an example, the $-\text{CH}$ -stretching vibration can be found in the narrow frequency range from 2880 to 2900 cm^{-1} . The exact location of the principal absorption band or bands of other chemical groups depends on the local chemical environment, especially the occurrence of intra- or intermolecular hydrogen bonding. In the case of the carbonyl group which can easily bond with hydrogen, absorption may occur over the broad range from 1700 to 1900 cm^{-1} . The presence of stereoisomers (i.e., tacticity and geometry isomers) may be identified by the appearance of new absorption frequencies, shifting of absolute frequencies, and band broadening in the infrared spectrum.

A good example of a typical FTIR spectrum is that shown in Figure 2-22 for the engineering thermoplastic, polycarbonate.



The IR-spectrum of this polymer is very distinctive. Principal absorption bands include those at 823 cm^{-1} (ring C-H bending), 1164 and 1231 cm^{-1} (C-O stretching), 1506 cm^{-1} (skeletal ring vibrations), and 1776 cm^{-1} (C=O stretching).

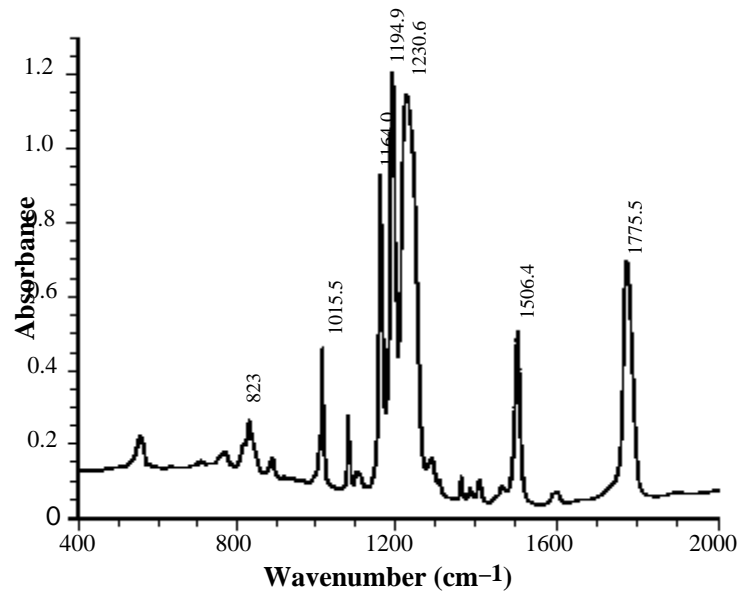
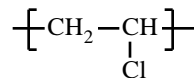


Figure 2-22 FTIR spectrum of a polycarbonate film.

The locations of IR absorbance peak maxima can also be sensitive to whether the chemical groups lie in crystalline lamellae (see Chapter 4) or in amorphous regions and, therefore, FTIR measurements can be used as a means to determine the degree of crystallinity of a sample. For example, FTIR-measurements can be used to follow the development of crystallinity in a sample of poly(vinyl chloride)



as a function of heat treatment. Commercial-grade PVC is a polymer of low crystalline order (ca. 7-10 % crystallinity). When heated above its glass transition temperature (87°C) and below its crystalline-melting temperature (212°C), the degree of crystallinity can be increased. One way of determining the percent of crystallinity is by density measurements (see Section 4.2.4). Another method is by quantitative measurements of the intensity of certain IR-absorbance peaks.

In the case of PVC, there are two principal overlapping absorbance peaks lying between 550 and 665 cm^{-1} and attributed to C-Cl stretching vibrations. One peak that appears to be crystalline sensitive is located at 635 cm^{-1} , while the other is crystalline insensitive and is located at 615 cm^{-1} . The ratio of the amplitude of the 635 - and 615-cm^{-1} peaks can, therefore, be used as a quantitative measure of the degree of crystallinity. This ratio is plotted as a function of crystallization time in Figure 2-23. As shown, the increase in the absorbance ratio closely follows the percent crystallinity determined from density measurements of the same samples.

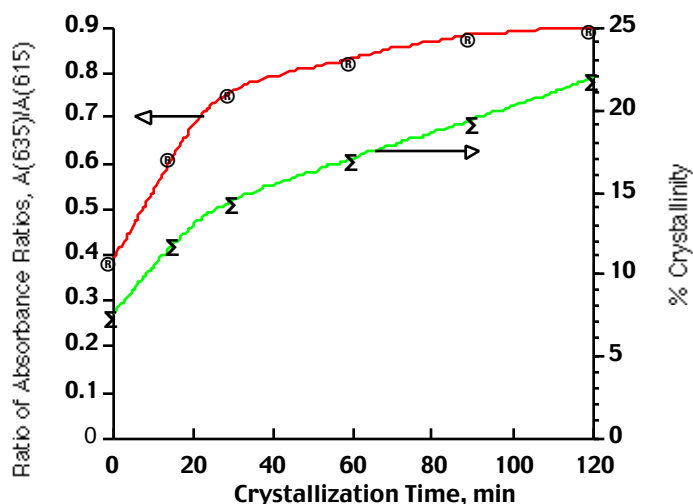


Figure 2-23 Plot of the ratio of the amplitudes of the FTIR absorbance peaks of poly(vinyl chloride) at 635 and 615 cm^{-1} as a function of crystallization time at 110° to 115°C .²⁷ Comparison is made to the percent crystallinity determined from density measurements.

Raman Spectroscopy. A technique related to infrared spectroscopy is Raman scattering, which results from a change in induced dipole moment or polarization of a molecule upon irradiation. In the case of Rayleigh scattering, there is no exchange of energy between the incident light and the molecule and therefore the scattered light has the same frequency, ν_R , as the incident light, ν_o . In Raman scattering, the molecule returns inelastically to an energy level different from the original state, and therefore the frequency of the scattered

light will be different (i.e., $\nu_R = \nu_o + \nu$). The strongest bands are those appearing at lower frequencies (i.e., the Stokes bands) and are the ones normally recorded. Perhaps the greatest advantage of Raman scattering in polymer characterization is that no special sample preparation is required, and therefore liquids and solids can be studied nondestructively. For this reason, Raman spectroscopy particularly lends itself to the study of polymer morphology, especially the study of crystalline structure and orientation effects.

2.6.2 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a very powerful technique for polymer characterization that can be used to determine tacticity, branching, structural defects such as the occurrence of head-to-head placement of monomers in vinyl polymers, the sequence of comonomer units in a copolymer chain, and chemical changes such as oxidation states, which can be detected at levels as low as one site per 500 repeat units. Although ^{13}C NMR is commonly used in polymer characterization, NMR measurements employing other NMR-active nuclei such as ^1H , ^{13}C , ^{17}O , and ^{19}F having magnetic moments may have an advantage in the study of some polymers.[†] For example, ^{29}Si NMR may be used in the characterization of polysiloxanes, ^{19}F NMR for fluoropolymers, ^{15}N NMR for polyamides, and ^{31}P NMR for polyphosphazenes. Two factors that contribute to relative sensitivity and utility of a particular nucleus in NMR spectroscopy are its natural abundance and gyromagnetic ratio (γ). The ^1H isotope with nearly 100% abundance and high gyromagnetic ratio is the most sensitive nucleus for NMR study. A listing of important NMR-active nuclei and their natural abundance is given in Table 2-10.

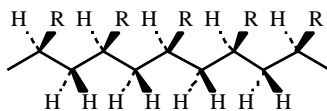
Two techniques of NMR measurements have been used in polymer studies. Broad-line NMR methods, usually proton relaxation, can be used to determine amorphous content and chain orientation in semicrystalline polymers. High-resolution NMR measurements can be used to obtain information concerning the sequence of repeating units in the chain; this enables the determination of tacticity and comonomer distribution, as described next.

[†] Any atomic nuclei having a *nonzero* spin quantum number, I , possess a magnetic moment. When placed in a magnetic field, these nuclei occupy $2I + 1$ quantized magnetic energy levels, called Zeeman levels. Transitions (resonance) between energy levels can occur by application of a resonant RF field of frequency ν_o (equal to the Larmor precession frequency). Resonance for a particular nucleus will occur at slightly different frequencies depending upon its chemical environment (i.e., its chemical bonding and position in the molecule) due to the shielding effect of electron clouds on a nucleus, which reduces the Larmor frequency. These frequency changes are termed *chemical shifts* and are given in reference to tetramethylsilane (TMS) as a standard. The range of chemical shifts is about 100 ppm for ^1H but more than 200 ppm for ^{13}C and other nuclei.

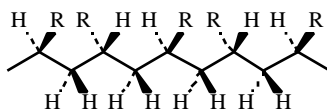
Table 2-10 Nuclei Used in Polymer NMR

Nuclei	Spin	Natural abundance (%)	Shift range (ppm)
^1H	1/2	99.985	15
^2H	1	0.0156	15
^{13}C	1/2	1.108	220
^{14}N	1	9.634	900
^{15}N	1/2	0.365	900
^{17}O	5/2	0.037	800
^{19}F	1/2	100	800
^{29}Si	1/2	4.70	250
^{31}P	1/2	100	700

Chemical Structure Determination by NMR Measurements. NMR measurements can provide a very detailed description of the chemical microstructure of a polymer chain, such as branching, head-to-head or head-to-tail addition, comonomer sequence, and tacticity, by measuring chemical shifts that are sensitive to the local environment (electron shielding) of a particular nucleus. For example, NMR measurements can be used to determine the isotactic content of a particular polymer. To understand NMR analysis of tacticity, it is useful to look at the spatial arrangement of several monomer units having an asymmetric substituent group, R. For a sequence of five monomer units, called a pentad, two extreme cases are possible, as discussed in Chapter 1. In an isotactic sequence, all the R groups lie on the same side of the chain as shown.

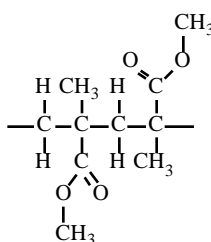


In this case, the four sequential pairs of monomer units (diads) are called meso (m) and, therefore, this particular pentad can be described as mmmm. For four repeating units (quartet), the sequence is represented as mmm and for three repeating units (triad), the sequence is represented as mm. In the case of syndiotactic chain structure, the substituent groups alternate from side to side as shown.



The sequence is all racemic (r) and the pentad can be described as rrrr. Correspondingly, the quartet is rrr and the triad is rr. The surrounding molecular environment can affect the chemical shift of the proton on a β -methylene (CH_2) group or a proton on the α -carbon substituent group. Whether the resolution can extend to triad, quartet, or pentad sequence identification depends upon the strength of the applied magnetic field.

A good illustration of the use of NMR measurements to determine polymer structure is poly(methyl methacrylate) (PMMA). Two repeating units (a diad) of an isotactic sample of PMMA are



If the polymer chain is syndiotactic, the two protons on the β -methylene groups are equivalent and, therefore, there should be a single resonance; however, if the chain is isotactic, the local environments (due to electron-cloud shielding) of the two protons are different, and four principal resonances (due to spin-spin interactions) result. NMR spectra for predominately syndiotactic and predominantly isotactic PMMA samples in 10% chlorobenzene at 135°C and observed at high frequency (220 MHz) are shown in Figure 2-24. The major peak intensity is assigned to the rrr quartet of the predominantly syndiotactic sample (Figure 2-24A) and four major peaks are assigned to the mmm quartet of the predominantly isotactic sample (Figure 2-24B).

Solid-State NMR. The spectral linewidth of solid samples is broad relative to that of liquids (0.2 to 5.0 Hz). This is because the relative immobility of molecules in the solid state results in stronger interactions compared to highly mobile molecules in the liquid state for which intramolecular interactions are averaged out. A technique that allows high-resolution NMR measurements of polymers in the solid state is called magic-angle spinning (MAS) NMR.²⁸ In this procedure, a cylindrical sample is rotated at high speed (>2 kHz) at an angle of 54.7° relative to the static field. Under these circumstances, linewidths decrease to those comparable to solution samples (~1 ppm). Solid-state NMR can be used to investigate the segmental mobility of polymer chains, the diffusion of small molecules in polymers, and polymer annealing and aging processes.

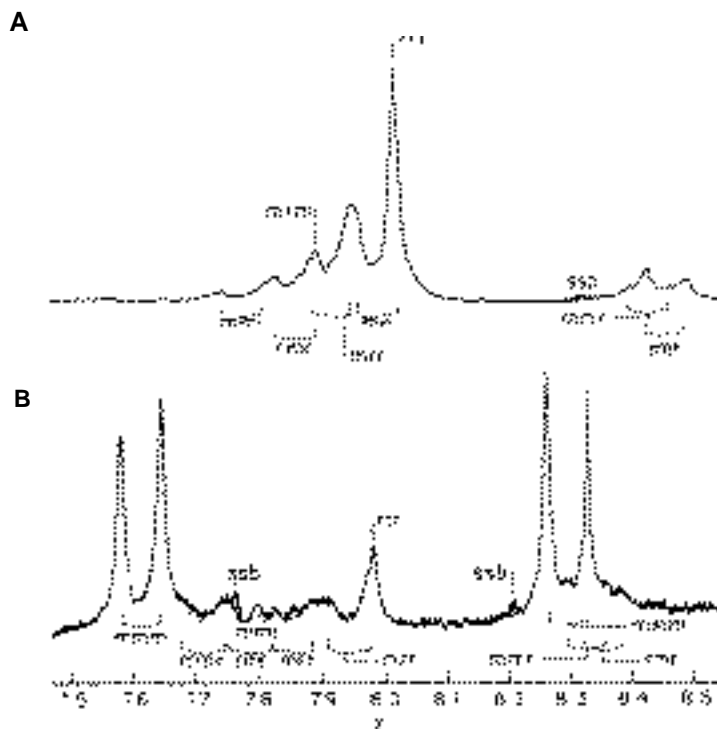


Figure 2-24 NMR spectra of the β -methylene proton for two samples of poly(methyl methacrylate) (PMMA) obtained in solution at 220 MHz. **A.** Predominantly syndiotactic PMMA. **B.** Predominantly isotactic PMMA. (Reprinted from *High Resolution NMR of Macromolecules*, F. A. Bovey, Copyright 1972, with permission from Elsevier.)

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Problems

2.1 What would be the number-average molecular weight of polystyrene obtained at the completion of an anionic (i.e., "living") polymerization in which 0.01 g of *n*-butyllithium and 10 g of styrene monomer are used? The molecular weights of butyllithium and styrene are 64.06 and 104.12, respectively.

2.2 Styrene is polymerized by free-radical mechanism in solution. The initial monomer and initiator concentrations are 1 *M* (molar) and 0.001 *M*, respectively. At the polymerization temperature of 60°C, the initiator efficiency is 0.30. The rate constants at the polymerization temperature are as follows:

$$k_d = 1.2 \times 10^{-5} \text{ s}^{-1}$$

$$k_p = 176 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_t = 7.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

Given this information, determine the following:

- (a) Rate of initiation at 1 min and at 16.6 h
- (b) Steady-state free-radical concentration at 1 min

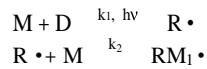
(c) Rate of polymerization at 1 min

(d) Average free-radical lifetime, τ , at 1 min, where τ is defined as the radical concentration divided by the rate of termination

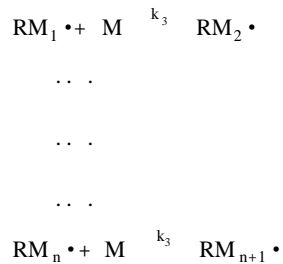
(e) Number-average degree of polymerization at 1 min

2.3 It has been reported that the rate of a batch *photopolymerization* of an aqueous acrylamide solution using a light-sensitive dye is proportional to the square of the monomer concentration, $[M]^2$, and the square root of the absorbed light-intensity, $I^{1/2}$. Note that, although this polymerization is free radical, the apparent kinetics appear not to be typical of usual free-radical polymerization for which the rate of polymerization is proportional to the first power of monomer concentration and to the square root of the initiator concentration (eq. 2.23). The following polymerization mechanism has been proposed to explain the observed kinetics:

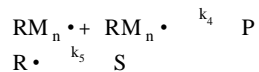
Initiation



Propagation



Termination



where

M, monomer

D, dye

P, terminated polymer

S, deactivated initiator

Show that this mechanism appears to be correct by deriving an equation for the rate of propagation in terms of $[M]$, I , and the appropriate rate constants. The following assumptions may be made:

1. Equal reactivity in the propagation steps
2. Steady-state concentration of $R\cdot$ and $RM_n\cdot$
3. $k_2 \ll k_5$
4. The concentration of dye, $[D]$, that has been activated by light and thereby contributes to the first initiation step is proportional to the absorbed light intensity.

2.4 Given the $Q-e$ values for styrene ($Q = 1.00$, $e = -0.8$) and 4-chlorostyrene ($Q = 1.03$, $e = -0.33$):

- (a) Calculate the reactivity ratios for styrene and 4-chlorostyrene.
- (b) Plot the instantaneous copolymer composition as a function of monomer concentration in the copolymerization mixture.
- (c) Comment on the expected monomer sequence distribution in the resulting copolymer.

2.5 If the number-average degree of polymerization for polystyrene obtained by the bulk polymerization of styrene at 60°C is 1000, what would be the number-average degree of polymerization if the polymerization were conducted in a 10% solution in toluene (900 g of toluene per 100 g of styrene) under otherwise identical conditions? The molecular weights of styrene and toluene are 104.12 and 92.15, respectively. State any assumptions that are needed.

2.6 Assume that a polyesterification is conducted in the absence of solvent or catalyst and that the monomers are present in stoichiometric ratios. Calculate the time (min) required to obtain a number-average degree of polymerization of 50 given that the initial dicarboxylic acid concentration is 3 mol L^{-1} and that the polymerization rate constant is $10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$.

2.7 Show how the assumption of steady-state free radical concentration, $\overline{M}_1\cdot$ or $\overline{M}_2\cdot$, can be used to obtain the instantaneous copolymerization equation in the form of eq. 2.42 starting with eq. 2.36.

2.8 Show that the ceiling temperature is a free-radical polymerization can be obtained as

$$T_c = \frac{-H_p}{R \ln(A_p[M]/A_{dp})}$$

2.9 Find the azeotropic composition for the free-radical copolymerization of styrene and acrylonitrile.

2.10 What polymer products would you expect to obtain in the free-radical copolymerization of styrene and vinyl acetate?

2.11 Explain why high pressure favors the propagation step in a free-radical polymerization. How would the rate of termination be affected by pressure?

2.12 From data available in Section 2.2.1, calculate the activation energy for propagation for the free-radical polymerization of styrene. Do you expect the activation energy to be dependent upon solvent in a solution polymerization?

2.13 Draw the chemical structures of the two ends of a terminated polystyrene chain obtained by the atom transfer radical polymerization of styrene using 1-PECL.

2.14 Show that the rate of polymerization in atom transfer radical polymerization is proportional to the equilibrium constant given in eq. 2.48.

2.15 Show that azeotropic copolymerization occurs when the feed composition is given as

$$f_1 = \frac{1 - r_1}{2 - r_1 - r_2}.$$

2.16 Methyl methacrylate is copolymerized with 2-methylbenzyl methacrylate (M_1) in 1,4-dioxane at 60°C using AIBN as the free-radical initiator.

(a) Draw the repeating unit of poly(2-methylbenzyl methacrylate).

(b) From the data given in the table below, estimate the reactivity ratios of both monomers.

f_1	F_1^*
0.10	0.14
0.25	0.33
0.50	0.52
0.75	0.70
0.90	0.87

* From ¹H-NMR measurements.